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Contribution from the Laboratory of General Chemistry of the University of Michigan.

THE RATE OF ACTION OF WATER ON CERTAIN α- β- AND γ-HALOGEN SUBSTITUTED FATTY ACIDS.

BY EDWIN DEBARR.

In the course of the investigations which were undertaken for the purpose of ascertaining the initial rate and limit of esterification of the halogen substituted fatty acids, it became evident that a study of the decomposition of these same substances by water was also necessary, with the object of fixing the lowest limit at which the change sets in. In following out this line, the necessity also soon showed itself of applying methods to this phase of the investigation similar to those developed in the study of esterification,[1] so that the research has practically changed into a determination of the velocity of the action of water on the substances in question.

The following acids came within the scope of the research: monochloracetic, dichloracetic, trichloracetic, α- and β-chlorpropionic, α-brompropionic, α-brombutyric, α-, β-, and γ-chlorbutyric, the object in treating the β- and γ-acids being to ascertain the influence of the distance of the halogen atoms from the carboxyl group, and in the case of the γ-acid, the effect of the tendency to form lactones displayed by the

[1] Lichty: This JOURNAL, 18, 590 (1896); Menschutkin: Ber d. chem. Ges., 11, 1507.

corresponding oxy-acid, which would be produced by hydrolysis.

During the course of the work it became necessary to somewhat modify the former methods of preparation of some of the substances investigated, the result being that in certain instances new boiling- and melting-points were observed for the absolutely pure products. The instances in which such modified methods were used are given below.

EXPERIMENTAL PART.

Preparation of β-Chlorpropionic Acid.

The β-chlorpropionic acid used in this investigation was prepared from β-iodopropionic acid,[1] the latter formed by a slight modification of the method of Victor Meyer.[2] In order to convert this product into pure β-chlorpropionic acid and obtain a good yield, it is essential to adhere closely to the following directions:

β-Iodopropionic acid is dissolved in almost ten times its own weight of water and chlorine is slowly passed in, the current being stopped from time to time and the contents of the flask thoroughly shaken until the odor of chlorine entirely disappears. The operation is complete when the gain in weight equals that required by theory. The iodine is then filtered off, the solution treated with sulphur dioxide until colorless, and then repeatedly extracted with ether.

After drying over calcium chloride and evaporating the solvent, the remainder is distilled several times over molecular silver, when all but a small trace of iodine is removed. The absolutely pure acid is then obtained by repeated recrystallization from ligroin. Its melting-point is 61°; its boiling-point is 204°; the previous melting-points[3] have been given from 35°.5–58°.

[1] Erlenmeyer: Ann. Chem. (Liebig), **191**, 284; Rosenthal: *Ibid*, **233**, 16 (1886); V. Meyer: Ber. d. chem. Ges., **19**, 3294; **21**, 24.

[2] The iodide of phosphorus is best made by dissolving 6.5 grams of yellow phosphorus in carbon disulphide and then slowly adding 50 grams of iodine, allowing to crystallize, and evaporating the carbon bisulphide in a vacuum. Pure garnet-red crystals, entirely free from iodine, are thus obtained, with the result that the subsequent addition of glyceric acid allows the reaction to go much more smoothly.

[3] Henry: J. prakt. Chem. [2], **31**, 127.

Preparation of β-Chlorbutyric Acid.

β-Chlorbutyric[1] acid was prepared by saturating an ethereal solution of crotonic acid with hydrochloric acid gas at 0°, sealing in a tube, and then allowing to stand at the temperature of the room for twenty-four hours. The tube was then opened, the ether evaporated, and the remainder dried in a desiccator, over lime and sulphuric acid, the final product being distilled at 22 mm. pressure, the boiling-point being 116°. On analysis this substance was found to be pure β-chlorbutyric acid, melting at 16°–16°.5.[2] [3]

Preparation of γ-Chlorbutyric Acid.

γ-Chlorbutyric[4] acid was made by saturating at 0°, with hydrochloric acid, an ethereal solution of trimethylenemonocarboxylic acid, placed in a tube which was sealed and allowed to stand forty-eight hours at the temperature of the room. At the end of this time the tube was opened, the ether evaporated, and the contents dried in a desiccator over lime and sulphuric acid, after which the residue was fractioned under diminished pressure, when it boiled at 196° (22 mm.).

[1] Karetnikow: J. Russ. Soc., **11**, 252; Pinner: Ber. d. chem. Ges., **12**, 2056; **17**, 2008; Michael and Freer: J. prakt. Chem. [2], **40**, 95 (1889).

[2] The crotonic acid used in preparing the β-chlorbutyric acid was made according to the following method: 10 grams of acetoacetic ester are dissolved in 250 cc. of water, placed in an Erlenmeyer flask, and surrounded by ice-water, 10 such flasks being treated at the same time. To each, gradually, soft or liquid sodium amalgam is added and then, from time to time, glacial acetic acid from a burette so that the solution at no time has other than a slightly alkaline reaction (a decided alkalinity or acidity is to be guarded against). When hydrogen passes through the mixture freely, the mercury is filtered, the whole acidified with concentrated sulphuric acid, and then distilled with steam. At first acetic acid, then oxybutyric acid, and finally, after continuing the operation for some time, crotonic acid comes over. All the distillates containing crotonic acid are shaken out with ether, the ether dried over calcium chloride, and evaporated, the acid being purified by recrystallizing it from ether. The distillates containing oxybutyric acid are neutralized with calcium carbonate and evaporated to dryness on a water-bath; concentrated sulphuric acid is then added to the calcium oxybutyrate, and the latter again distilled with superheated steam, by which means a further quantity of crotonic acid can be isolated. In this manner 40 grams of crotonic acid were obtained from 100 grams of acetoacetic ester.

[3] The absence of α-acid was proved by decomposing the β-chlor acid by carefully boiling with aqueous potash, added gradually until the solution was permanently alkaline. It was then acidified, extracted with ether, the solution dried, and the solvent evaporated. Almost all of the remainder crystallized to *crotonic acid* (m. p. 71°), the crystals were filtered off by a filter-pump, and the remaining syrup boiled with zinc carbonate, filtered, and evaporated. The zinc salt was entirely amorphous, demonstrating the absence of α-oxybutyrate.

[4] Henry: Bull. Soc. Chim. (Paris), **45**, 341.

On analysis the substance was found to be pure γ-chlorbutyric acid, melting at 12°.

Method of Investigation.

At the outset it was necessary to determine the temperature at which water begins to act upon the chloracetic acids. This investigation was carried on in sealed tubes of from 5 to 8 cc. capacity. Approximately 0.1 gram of water was introduced into each of several thin-walled, glass bulbs of about 1 cc. capacity, and each was then sealed. One of these bulbs was inserted into a tube, a molecular amount of acid introduced, and the larger tube sealed by drawing to a thin point, the first set of determinations being made with 1 molecule of water to 1 molecule of monochloracetic acid. The small bulb on the inside was broken in each case by shaking, and the tube was then immediately immersed in a bath of boiling water, and heated for a given time. It was then rapidly cooled by dipping into vessels containing water of different degrees of temperature, after which the amount of acid changed was immediately estimated. It was found that below 110° there was practically no change with 1 molecule of water to 1 molecule of monochloracetic, α-chlorpropionic, or α-brombutyric acids.

In the study of di- and trichloracetic acids 2 and 3 molecules, respectively, of water were used, and, although decomposition took place more readily with these acids, it was, nevertheless, necessary to use a higher temperature with the others, so that all were finally decomposed at 150°. For this purpose a glycerine-bath of about 10 kilograms' capacity was employed, the various tubes being suspended therein while being heated. A gas-regulator consisting of a mercurial portion outside of the bath connected with a bulb of about 200 cc. capacity, submerged in the glycerin, was used, the gas being supplied to the mercurial portion from a gas-regulator of the pattern described by Murrill.[1] The tubes prepared for investigation, with the inside bulbs broken, were suspended by means of wires in the glycerin, and the time of their introduction noted. At no time during the investigation did the

[1] J. Am. Chem. Soc., **20**, 501.

temperature fall below 149°, nor did it rise above 150°. The temperature was observed every fifteen minutes during the investigation of any acid.

In every case, except trichloracetic acid, the amount of acid transformed was estimated by a tenth-normal solution of silver nitrate with yellow potassium chromate as indicator, the free organic acid as well as the hydrochloric acid being removed by sodium or potassium acetate.

When the proper time came for taking out any tube, it was dipped into boiling, then hot, then warm, and finally into cold water. The small point was broken off under water in the vessel in which the estimation of hydrochloric acid was to be made, and the amount of the latter substance determined as soon as possible.

In the case of trichloracetic acid a variation from the above-mentioned method was resorted to, for the amount decomposed was estimated by difference, the determination of the acid not transformed being by use of a tenth-normal solution of barium hydroxide with methyl orange or phenolphthalein as indicator.

Results Obtained with Monochloracetic Acid at 150°.

The following results were obtained with 1 molecule of water and 1 molecule of monochloracetic acid at 150° C.

Time in hours.	Per cent of acid transformed.
½	1.01
1	1.74
2	2.01
3	3.77
4	5.45
5	5.72
6	5.87
7	6.90
8	7.37
9	7.44
10	7.65
15	19.65
20	24.41
30	20.76

After thirty hours the tubes, on being opened, began to show pressure and the contents became dark, the amount of

acid apparently transformed being then less than at twenty hours, showing that by-products were being formed which absorbed hydrochloric acid and altered the nature of the reaction. As the amount of hydrolysis was limited when only 1 molecule of each substance was heated, it was necessarily decided to investigate the rate of action of 2 molecules of water to 1 molecule of monochloracetic acid, and the following results were obtained :

Time in hours.	Per cent of acid transformed.
1	6.08
2	9.71
3	12.60
4	14.24
5	13.58
6	18.83
7	10.27
8	26.28
9	28.35
10	28.20
15	36.38
20	44.33

At the end of twenty-four hours the tubes showed pressure. This amount of water did not give the results hoped for. The investigation was changed, 3 molecules of water being used to 1 molecule of monochloracetic acid. The results are given in the following table : (See Figure 1.)[1]

Time in hours.	Per cent of acid transformed.	Average per cent.
½	3.98	4.06
	4.14	
1	8.63	8.59
1	8.55	
2	15.78	14.46
2	13.13	
3	25.26	25.23
3	25.19	
4	29.76	29.30
4	28.83	
5	34.39	33.89
5	33.39	
6	36.80	36.90
6	37.00	

[1] In all the figures except 3 the curves are drawn on the basis of time in hours.

Time in hours.	Per cent of acid transformed.	Average per cent.
7	40.70	40.71
7	40.71	
8	41.00	41.10
8	41.20	
9	41.08	41.20
9	41.31	
10	41.31	41.32
10	41.32	
15	41.29	41.33
15	41.36	
20	43.93	43.85
20	43.78	
24	46.07	46.50
24	46.92	
30	47.03	47.03
30	47.03	

The tubes that were heated more than thirty hours exhibited pressure. Owing to these results and for the sake of comparison it was now decided to treat 1 molecule of each acid with 3 molecules of water for each chlorine atom present.

Rate of Action of Dichloracetic Acid and Water at 150°.

Dichloracetic acid was heated with 6 molecules of water to 1 molecule of the acid, and the following results were obtained: (See Figure 2.)

Time in hours.	Per cent of acid transformed.	Average per cent.
½	5.31	5.32
½	5.33	
1	7.91	7.93
1	7.94	
2	12.16	12.17
2	12.17	
3	13.61	13.52
3	13.43	
4	15.88	16.01
4	16.21	
5	17.80	17.76
5	17.71	

The tubes that were heated for six hours gave evidence of pressure when they were opened.

Dichloracetic acid was also heated with 8, 10, 12, and 18

molecules of water, respectively, to 1 molecule of the acid. In each case carbon was set free and the tubes exhibited pressure in less than ten hours.

One feature of interest presented itself here as well as in the case of the monochloracetic acid. The size of the tube as compared with the amount of the acid used seemed to affect the amount of transposition, for the duplicates containing the smaller amount of acid in proportion to the size of the tubes always gave the higher result.

Rate of Action of Water with Trichloracetic Acid at 150° C.

One molecule of trichloracetic acid was heated with 9 molecules of water with the following results: (See Figures 3 and 4.)

Time.	Per cent of acid transformed.	Average per cent.
5 min.	6.41	6.33
5 "	6.24	
10 "	13.20	13.45
10 "	13.70	
15 "	22.80	22.80
15 "	22.79	
20 "	27.67	27.68
20 "	27.68	
24 "	31.74	31.74
24 "	31.74	
30 "	42.50	42.38
30 "	42.25	
45 "	51.60	51.85
45 "	52.10	
1 hr.	79.83	79.92
1 "	80.01	
1½ hrs.	92.34	92.23
1½ "	92.11	
1⅔ "	92.24	92.67
1⅔ "	93.10	
1¾ "	95.23	95.30
1¾ "	95.36	
2 "	96.26	96.18
2 "	96.10	
3 "	97.20	97.21
3 "	97.22	
4 "	98.54	98.54
4 "	98.54	

Time.	Per cent of acid transformed.	Average per cent.
5 hrs.	98.60	98.60
5 "	98.60	
6 "	98.70	98.75
6 "	98.80	
7 "	99.40	99.40
7 "	99.39	
8 "	100.00	100.00
8 "	100.00	

Rate of Action of α-Chlorpropionic Acid with Water at 150° C.

One molecule of α-chlorpropionic acid was heated with 3 molecules of water and the following results were obtained: (See Figure 5.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	4.45	4.42
½ "	4.39	
1 "	6.21	6.22
1 "	6.23	
2 hrs.	8.98	8.70
2 "	8.42	
3 "	11.97	11.41
3 "	10.84	

Tubes heated longer than three hours showed pressure.

Rate of Action of α-Brompropionic Acid with Water at 150° C.

α-Brompropionic acid was heated with 3 molecules of water with the following results: (See Figure 6.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	2.89	2.93
½ "	2.97	
1 "	5.29	5.31
1 "	5.33	
2 hrs.	7.13	7.06
2 "	6.99	

Tubes heated longer than two hours showed pressure.

Rate of Action of α-Chlorbutyric Acid with Water.

α-Chlorbutyric acid was heated with 3 molecules of water with the following results: (See Figure 7.)

Time.	Per cent of acid transformed.	Average per cent.
¼ hr.	1.80	1.90
¼ "	2.00	
½ "	5.80	5.80
½ "	5.80	
1 "	6.40	6.50
1 "	6.60	
2 hrs.	7.01	7.02
2 "	7.03	
3 "	7.50	7.50
3 "	7.50	

The tubes that were heated longer than three hours gave evidence of pressure.

Rate of Action of α-Brombutyric Acid with Water at 150° C.

α-Brombutyric acid was heated with 3 molecules of water and the following results were obtained: (See Figure 8.)

Time.	Per cent of acid transformed.	Average per cent.
½ hr.	3.76	3.77
½ "	3.77	
1 "	5.78	5.80
1 "	5.81	
2 hrs.	7.29	7.27
2 "	7.24	
3 "	9.24	9.25
3 "	9.26	

The tubes which were heated more than three hours gave evidence of pressure.

Rate of Action of β-Chlorpropionic Acid with Water at 150° C.

β-Chlorpropionic acid was heated with 3 molecules of water to 1 of acid and the following results were obtained: (See Figure 9.)

Time.	Per cent of acid transformed.	Average per cent.
5 min.	18.21	18.26
5 "	18.30	
10 "	23.00	23.23
10 "	23.46	
15 "	39.97	40.44
15 "	40.90	
30 "	41.30	41.50
30 "	41.70	

Time.	Per cent of acid transformed.	Average per cent.
1 hr.	43.71	43.57
1 "	43.42	
2 hrs.	47.16	47.33
2 "	47.50	
3 "	49.25	49.44
3 "	49.63	
4 "	50.16	50.49
4 "	50.81	

Tubes that were heated more than four hours gave evidence of pressure.

Rate of Action of β-Chlorbutyric Acid with Water at 150° C.

Three molecules of water were heated with 1 molecule of β-chlorbutyric acid with the following results: (See Figure 10.)

Time.	Per cent of acid transformed.	Average per cent.
2 min.	1.52	1.92
2 "	2.32	
5 "	2.65	2.41
5 "	2.17	
10 "	4.15	4.22
10 "	4.29	
15 "	12.48	12.74
15 "	13.00	
30 "	30.29	29.97
30 "	29.65	
1 hr.	35.50	35.70
1 "	35.90	
2 hrs.	36.46	36.96
2 "	37.45	
3 "	37.36	37.38
3 "	37.40	

Tubes that were heated longer than three hours gave evidence of pressure.

Rate of Action of γ-Chlorbutyric Acid with Water at 150° C.

When γ-chlorbutyric acid is heated with 3 molecules of water to 1 of the acid the transformation is complete in five minutes, the action being so rapid that the curve showing the rate cannot be determined with any degree of accuracy.

The effect produced by the varying size of the tubes to which attention was called under the heads of mono- and di-

chloracetic acids was noticed throughout the work with the other acids, for the duplicate having the larger capacity with a proportionally smaller amount of acid invariably gave the higher figures, while these tubes which were of the same capacity and contained the same amount of acid invariably gave concordant results. In all instances the external conditions were absolutely unvarying ; the differences could therefore only be due to the variations in the size of the tubes. In the tables the duplicate result represents that with the larger tube.

Comparison of Results.

We find, by comparing the rates of action of the various acids with water, the following results :

Acid.	Per cent of transformation. One-half hour.	One hour.
Monochloracetic	4.06	8.59
Dichloracetic	5.32	7.93
Trichloracetic	42.38	79.92
α-Chlorpropionic	4.42	6.22
α-Brompropionic	2.93	5.31
α-Brombutyric	3.77	5.80
α-Chlorbutyric	5.80	6.50
β-Chlorpropionic	41.50	41.50
β-Chlorbutyric	29.97	35.70
γ-Chlorbutyric	100.00	100.00

Acid.	Per cent of transformation.	Time transformation ceases.
Monochloracetic	47.11	30 Hrs.
Dichloracetic	17.76	5 "
Trichloracetic	100.00	8 "
α-Chlorpropionic	11.41	3 "
α-Brompropionic	7.06	2 "
α-Brombutyric	9.25	3 "
α-Chlorbutyric	7.50	3 "
β-Chlorpropionic	50.49	4 "
β-Chlorbutyric	37.38	3 "
γ-Chlorbutyric	100.00	5 Min.

The lowest limit at which the regular run of the reaction ceases and at which decomposition sets in is to be found with α-brompropionic acid. So that, for purposes of comparison, it is perhaps best to construct a table showing the time limit at which, in each case, 7 per cent has been transposed. The results are as follows :

	Acid.	7 per cent.	18 per cent.
1	γ-Chlorbutyric	Few sec.	Few sec.
2	β-Chlorpropionic	1 min.	5 Min.
3	Trichloracetic	6 "	12 "
4	β-Chlorbutyric	11 "	20 "
5	Monochloracetic	45 "	30 "
6	Dichloracetic	60 "	
7	α-Chlorpropionic	75 "	
8	α-Brompropionic	120 "	
9	α-Brombutyric	120 "	
10	α-Chlorbutyric	120 "	

Based upon this table, the order of affinity for the above acids would be :

1 γ-Chlorbutyric acid.
2 β-Chlorpropionic acid.
3 Trichloracetic acid.
4 β-Chlorbutyric acid.
5 Monochloracetic acid.
6 Dichloracetic acid.
7 α-Chlorpropionic acid.
8 α-Brompropionic acid.
9 α-Brombutyric acid.
10 α-Chlorbutyric acid.

The affinity constants of these acids,[1] so far as they have been determined, are as follows :

Acid.	K.
Acetic	0.0018
Monochloracetic	0.155
Dichloracetic	5.1
Trichloracetic	121.0
α-Brompropionic	0.108
β-Brompropionic	0.0098
α-Brombutyric	0.106

So that the order in which decomposition takes place is, excepting in the cases of mono-, di-, and trichloracetic acids, not the same as is that of the affinity constants.

The acids begin to break down, giving pressure in the tubes, when the following per cents have entered into reaction :

[1] Walden : Ztschr. phys. Chem., **10**, 563, 638.

Acid.	Per cents.	Time.
α-Brompropionic	7.06	2 hrs.
α-Chlorbutyric	7.50	3 "
α-Brombutyric	9.25	3 "
α-Chlorpropionic	11.41	3 "
Dichloracetic	17.76	5 "
β-Chlorbutyric	37.38	3 "
Monochloracetic	47.11	30 "
β-Chlorpropionic	50.49	4 "
Trichloracetic	100.00	8 "
γ-Chlorbutyric	100.00	5 min.

This is then the stability of the compounds at 150°, under pressure and in the presence of hydrochloric acid. The interesting fact is then developed that the order of stability is the same as that of the affinity. In other words, the acids which are most stable react the most rapidly, and those which are least stable react the most slowly.

The time limit of the transposition of the various acids is affected by the number of carbon atoms in 1 molecule in the respective acids, so that the time becomes markedly less in passing from the derivatives of acetic acid to the next higher homologues. This is especially apparent with the α-monochlor acids. Thus chloracetic acid reaches its limit in thirty hours, α-chlorpropionic in three hours, and α-chlorbutyric acid in three hours.

Examining the β-acids we find that β-chlorpropionic acid reaches its limit in four hours, while β-chlorbutyric acid does so in three hours, a result similar to that observed with the α-acids.

We have observed no other γ-acid with which to make a comparison. We need not take the limit to make these comparisons, but if we observe the transformation of the various acids at the end of one hour, the same observations are true as to amounts. The greater the number of carbon atoms in the α-acids passing from acetic acid to the next higher homologues the less is the amount of acid transformed at the end of one hour. The same law holds true in the case of the β-acids.

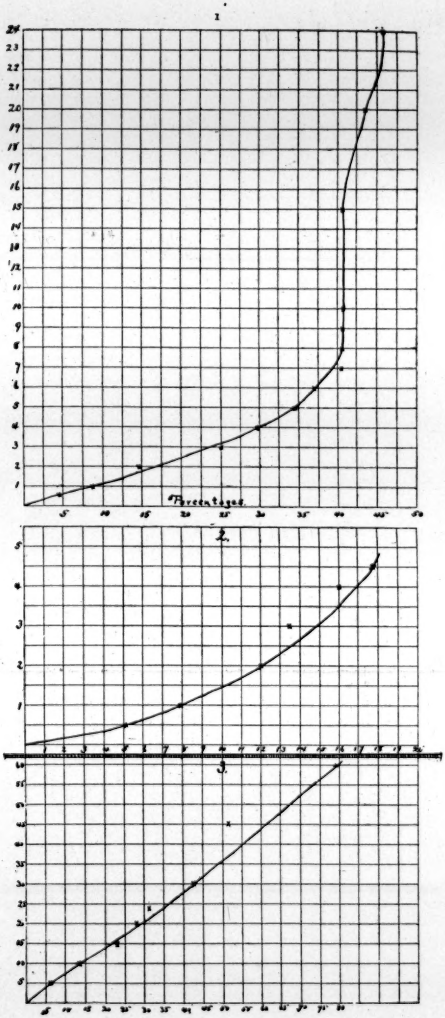
In discussing the influence of distance of halogen from the carboxyl group, the most interesting fact is that the rate of transposition rapidly increases, the further the halogen atom,

in any given molecule, is, according to our present views, removed from the carboxyl group. This is notably the case with α-chlorpropionic (4.42 per cent after one-half hour) and β-chlorpropionic acids (41.5 per cent after one-half hour) and with α-brombutyric (3.77 per cent), β-chlorbutyric (29.97 per cent), and γ-chlorbutyric acids (100 per cent). This result would not be surprising with γ-acids, as the tendency to form lactones would there play a prominent part, but this same reason cannot be alleged in the case of the β-acids, where there is an equally marked increase. So far as the work has gone, therefore, it would seem that the further a halogen atom is removed from the carboxyl group, the greater the influence of the latter on its reactivity, or, to put the matter in a different form, the protective action of the carboxyl group, if it exists, diminishes as the distance of the halogen, according to our present views, increases. It would be interesting to follow the influence also, in the cases of δ- and ω-acids, but the difficulty of preparing the latter in the pure state has hitherto stood in the way; the investigation will, however, be continued along this line.

So far, none of the reactions given above have been capable of being reduced to mathematical formulæ, and, indeed, more data are required before this can be successfully accomplished. Work on the esterification of these acids, as well as on the affinity constant, is now being conducted in this laboratory, with the ultimate object of combining all results so as to be able, if possible, to determine accurately the meaning of the term distance of the halogen from the carboxyl group.

The only previous work along these lines was done by Schwab,[1] who investigated the action of sodium hydroxide solution on monochloracetic acid in such a way that, while the amount of alkali remained constant, the solvent water was increased; it developed that the rate became greater as the amount of water increased, so that the rate depended upon the ionization of the acid. If this is true with monochloracetic acid, the cause of the differing reactive velocities noted alone may also be found in the degree of ionization. This question will be settled by the determination of the affinity constants.

[1] Schwab: Inaugural dissertation, Amsterdam, 1883.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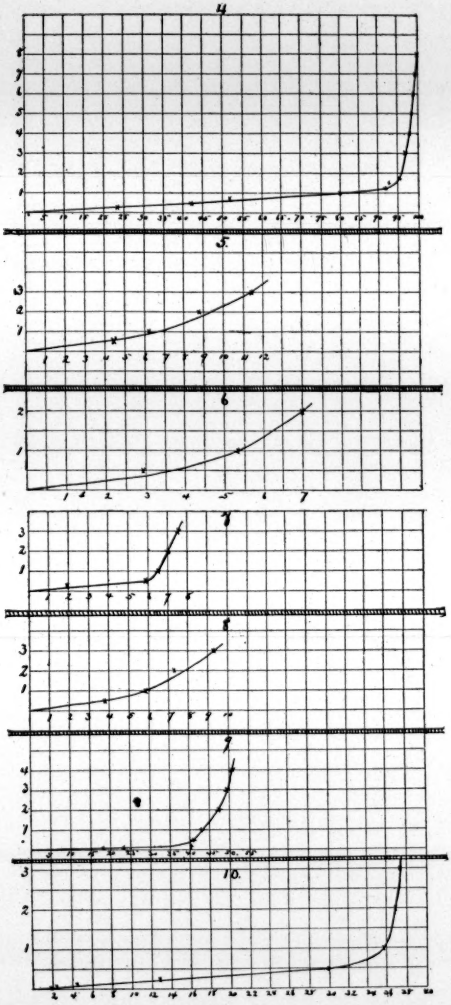
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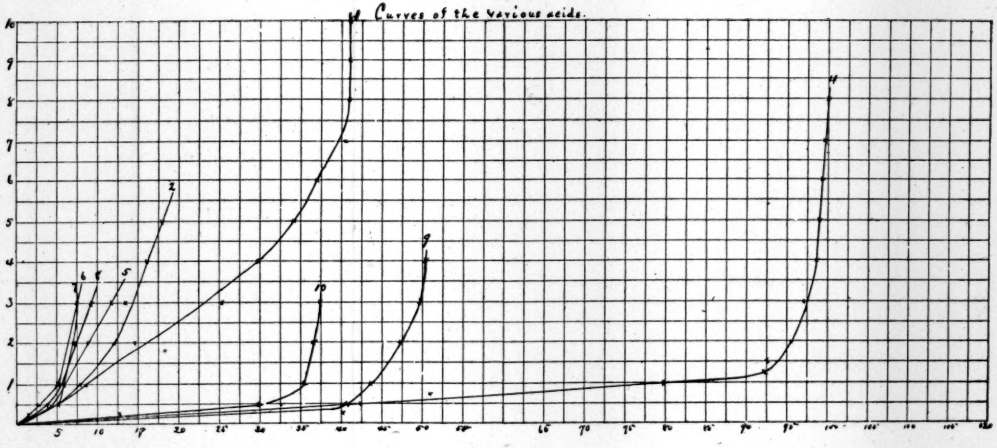
Curves of the various acids.

Contributions from the Chemical Laboratory of Harvard College.

CXV.—THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.[1]

By Gregory Paul Baxter.

In the course of the work upon the atomic weight of cobalt, described in preceding papers from this laboratory,[2] it became necessary to weigh metallic cobalt which had been reduced from the bromide and from the oxide by means of hydrogen. A few experiments were made at the time to show that the metal in question did not occlude appreciable amounts of hydrogen, but the comparison of this result with the conflicting accounts of others showed that the subject was worthy of further attention.

Hempel and Thiele,[3] by quantitative combustion of metal reduced from the oxide at a high temperature, obtained no water. Neumann and Streintz,[4] on the other hand, also working with material obtained from the oxide, found that their cobalt occluded in one case 150 times, in another 50 times, its volume of hydrogen. Troost and Hautefeuille[5] determined the occluded hydrogen by heating the metal in a vacuum and measuring the gas evolved. Ingots of cobalt, after ignition in hydrogen, yielded only 0.1 their volume of occluded gas; foil obtained by electrolysis evolved 35 volumes of hydrogen, and upon heating in hydrogen was found to have taken up 24 volumes, while powdery cobalt, obtained by reduction of the oxide, evolved 100 times its volume of hydrogen. This latter preparation proved to be pyrophoric in air, even after the hydrogen had been removed. Neumann and Streintz also observed the same property in their cobalt when exposed to an atmosphere of oxygen.

Although this evidence seems contradictory at first sight, in reality much can be said on both sides. Metallic cobalt

[1] The investigation on the atomic weight of cobalt, of which this paper formed a part, was presented to the Faculty of Arts and Sciences of Harvard University as a thesis for the degree of Ph.D., in 1899.

[2] Richards and Baxter: Proc. Amer. Acad., **33**, 115 (1897); **34**, 351 (1899); **35**, 61 (1899).

[3] Zeit. anorg. Chem., **11**, 93.

[4] Monatsh. Chem., **12**, 642.

[5] Compt. rend., **80**, 788.

shows widely different characteristics in its behavior toward hydrogen according to its purity and the method by which it is prepared. In some cases the present work shows it to have occluded only traces of hydrogen or none at all; in others it occluded amounts comparable with those found by Neumann and Streintz, and Troost and Hautefeuille.

In the following experiments the occluded hydrogen was determined by the method already mentioned;—combustion of the metal and determination of the water formed. For this purpose the following apparatus was used:

Three columns of beads moistened with strong sulphuric acid were followed by a tube containing phosphoric anhydride. These were connected with a combustion tube which contained the boat with the metal under examination and beyond the boat a coil of copper oxide. This copper oxide was prepared by igniting a roll of copper gauze in oxygen. Beyond this apparatus was a weighed phosphoric pentoxide tube, and this in turn was connected with an aspirator through an unweighed safety drying tube.

Owing to the fact that the organic matter emanating from rubber upon combustion will yield water, rubber was wholly avoided in this apparatus with the exception of the connections necessary for making attachment to the combustion tube. All other joints were made wholly of glass.

After the introduction of the boat containing the cobalt into the combustion tube, and before the absorption bulb was attached, a slow current of air was drawn through the tube for some time, while the copper oxide was heated to dull redness. The weighed bulb was then inserted in the circuit and the section of the tube containing the boat was heated until oxidation of the metal took place. In order to avoid removal of oxygen from the air which should finally fill the absorption bulb, the current of air was continued until the boat had become cool.

After each analysis the phosphoric anhydride bulb, which could be closed by means of glass stop-cocks, was wiped with a damp cloth and allowed to stand in the balance-case one-half hour. Needless to say, before the bulb was weighed the pressure inside and out was equalized by opening one of the

stop-cocks. As the time between two successive weighings was never more than two hours and usually not more than one, atmospheric conditions did not change sufficiently to necessitate weighing the bulb by substitution, so this precaution was omitted.

Several blank experiments were carried out in which the average gain in weight of the bulb per hour was 0.2 gram. In another case a tube, the volume of which was 13.0 cc., filled with pure hydrogen at the room temperature, was inserted in the apparatus and the water formed by the combustion of the hydrogen was collected in the bulb. The weight of the water formed in two experiments was 0.0111 gram and 0.0107 gram, while theory required 0.0108 gram. Evidently the apparatus was effective for its purpose.

In several instances which have already been described,[1] pure cobalt reduced from the bromide was heated to 500° in a hard glass tube, from which the air had previously been completely exhausted by a Sprengel air-pump. In no case was a measurable quantity of gas evolved and the cobalt did not lose in weight. Although at the time the evidence seemed sufficient to show that this cobalt did not possess the property of occluding important amounts of hydrogen when heated in this gas, a few grams of metal reduced from the bromide were subjected to quantitative combustion. In calculating the volumes of occluded hydrogen given under the following analyses, the specific gravity of cobalt is assumed to be 8.5, and the weight of a liter of hydrogen, at 20° and 760 mm. pressure, to be 0.0839 gram.

I. 2.5 grams of cobalt yielded 0.0005 gram of water, or 2.0 volumes of hydrogen.

II. 2.5 grams of cobalt yielded 0.0010 gram of water, or 4.0 volumes of hydrogen.

III. 2.5 grams of cobalt yielded 0.0004 gram of water, or 1.6 volumes of hydrogen.

In analyses II and III the original cobalt was reduced and reoxidized, and it can be seen that this treatment produced no appreciable effect upon the amount of the occluded hydrogen. It was evident that cobalt reduced from the bromide does not

[1] Proc. Amer. Acad., 34, 355.

possess the property of occluding hydrogen to an important extent.

On the other hand, cobalt reduced originally from the oxide was found to contain amounts of hydrogen varying widely with the purity and the method of preparation. Cobalt oxide, free from alkalies and silica, was obtained by dissolving electrolytic metal in the purest nitric acid and precipitating the cobalt as hydroxide by the addition of pure redistilled ammonia, all in platinum vessels. No attempt was made to remove other impurities, since these could not have been present in sufficient quantities to produce an appreciable effect. This oxide was reduced in hydrogen at 400°–500°, and the metal was subjected to combustion as soon as cold. The weight of cobalt given is somewhat higher than it should be, owing to the fact that it is impossible to obtain complete reduction at the temperature employed. It will be shown later that a temperature sufficiently high to produce complete reduction alters the behavior of the metal toward hydrogen.

IV. 2.0 grams of cobalt yielded 0.0034 gram of water, or 19 volumes of hydrogen.

V. 6.4 grams of cobalt yielded 0.0105 gram of water, or 19 volumes of hydrogen.

VI. 2.9 grams of cobalt yielded 0.0053 gram of water, or 21 volumes of hydrogen.

As has already been suggested by Richards and Cushman,[1] the cause of this great difference in behavior might be explained by either of two hypotheses. The sodic bromide contained in the cobaltous bromide might be the agent which prevented the occlusion in the case of metal reduced from the bromide, or the volatility of the cobaltous bromide might allow the reduced metal to be deposited in a form essentially different from that reduced from the oxide. Two simple experiments served to decide this dilemma. In the first place the same 2.5 grams of cobalt reduced from the bromide were leached with pure water until all soluble matter had been removed. After drying and heating in hydrogen the metal was again subjected to combustion.

VII. 2.5 grams of cobalt yielded 0.0004 gram of water, or 1.6 volumes of hydrogen.

[1] Proc. Amer. Acad., 34, 333.

The first conception that the sodic bromide protected the reduced metal was evidently at fault. Furthermore, cobalt oxide that had been precipitated in the presence of much sodic chloride by means of sodic hydrate, and which consequently contained a large amount of alkaline and siliceous impurity, was reduced as usual with the intention of determining the effect of this alkali. Upon removing the boat containing the metal from the reduction tube spontaneous oxidation took place, and it was found necessary to replace the hydrogen in the reduction tube, after it was cool, by nitrogen and to insert the tube bodily between the drying train and the combustion tube. This cobalt differed from the samples previously examined in that it did not contract or "sinter" to any extent. Whether this effect was due to the alkalies or to silica is uncertain.[1] One determination of the hydrogen occluded by metal treated in this way was made.

VIII. 2.0 grams of cobalt yielded 0.0085 gram of water, or 48 volumes of hydrogen.

Evidently the impurities did not protect the cobalt from the hydrogen, hence one is driven to accept the second solution of the dilemma, and to decide that cobalt reduced from the bromide differs in its state from that obtained from the oxide.

The experiment already described of heating in a vacuum cobalt reduced from the bromide was now repeated with metal obtained from the oxide. In every case gas was evolved during this process, as would have been expected, and the metal upon combustion proved to contain only traces of hydrogen.

IX. 2.7 grams of cobalt yielded 0.0008 gram of water, or 3.5 volumes of hydrogen.

X. 5.0 grams of cobalt yielded 0.0010 gram of water, or 2.5 volumes of hydrogen.

XI. 5.0 grams of cobalt yielded 0.0014 gram of water, or 3.2 volumes of hydrogen.

That no appreciable amount of hydrogen was given off at ordinary temperatures was evident from the following analyses. The cobalt was placed in a hard glass tube, which was

[1] Richards and Cushman found that nickel which had been "purified" in glass vessels contained enough of these two impurities to prevent its sintering when reduced in hydrogen (Proc. Amer. Acad., 34, 328).

then exhausted, while cold, with a Sprengel air-pump. After this treatment it was subjected to combustion as usual (Analyses XII and XIII), and the oxide remaining from the combustion was again reduced and the metal analyzed for hydrogen as soon as cold (Analyses XIV and XV). It can be seen that the amounts of hydrogen obtained in the two cases are essentially the same.

XII. 2.5 grams of cobalt yielded 0.0017 gram of water, or 7.6 volumes of hydrogen.

XIII. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XIV. 2.5 grams of cobalt yielded 0.0019 gram of water, or 8.6 volumes of hydrogen.

XV. 2.7 grams of cobalt yielded 0.0029 gram of water, or 12.3 volumes of hydrogen.

This was further shown by passing dry air first over cold freshly reduced metallic cobalt and then over hot copper oxide. The small amount of water formed was collected in the usual way, and is entirely in agreement with the preceding results.

XVI. 2.0 grams of cobalt yielded 0.0006 gram of water in one hundred and fifty minutes.

Troost and Hautefeuille, however, found that cobalt which contained one hundred times its volume of hydrogen gave up a considerable part of it in a vacuum without the application of heat.

In several analyses in which cobalt was allowed to stand in hydrogen for at least twenty-four hours at the room temperature, the amount of water obtained upon combustion was considerably larger than that obtained from metal which was subjected to combustion immediately after reduction.

XVII. 2.7 grams of cobalt yielded 0.0160 gram of water, or 68 volumes of hydrogen.

XVIII. 2.9 grams of cobalt yielded 0.0117 gram of water, or 46 volumes of hydrogen.

The metal of Analysis XVIII, when analyzed immediately after reduction, yielded 0.0053 gram of water.

In order to show that this difference was not due to a change in the metal itself (owing to the process of oxidation

and reduction), equal amounts of the same preparation of oxide were reduced under conditions exactly similar. One sample (Analysis XIX) was allowed to stand in hydrogen at the room temperature for twenty-four hours; the other sample (Analysis XX) was subjected to combustion as soon as cold.

XIX. 2.3 grams of cobalt yielded 0.0043 gram of water, or 21 volumes of hydrogen.

XX. 2.3 grams of cobalt yielded 0.0022 gram of water, or 11 volumes of hydrogen.

From this fact that long-continued standing in cold hydrogen increases the amount of gas occluded, it is evident that cobalt possesses the property of taking up hydrogen at ordinary temperatures. This occlusion progresses only slowly in the cold, however, for the amount taken up in twenty-four hours was less than that occluded during ordinary reduction and cooling. In the following cases the metal was first heated in a vacuum and then allowed to stand in an atmosphere of hydrogen for twenty-four hours at the room temperature.

XXI. 2.7 grams of cobalt yielded 0.0020 gram of water, or 8.5 volumes of hydrogen.

XXII. 2.7 grams of cobalt yielded 0.0018 gram of water, or 7.5 volumes of hydrogen.

The same metal, after reduction and cooling in hydrogen, yielded 0.0035 gram of water.

Cobalt reduced in hydrogen and allowed to cool in pure nitrogen occluded only traces of hydrogen.

XXIII. 1.9 grams of cobalt yielded 0.0004 gram of water, or 2.1 volumes of hydrogen.

XXIV. 1.9 grams of cobalt yielded 0.0010 gram of water, or 5.4 volumes of hydrogen.

This same cobalt, when cooled in hydrogen, yielded 0.0029 gram of water upon combustion, or nearly 16 volumes of hydrogen.

According to Neumann and Streintz, repeated oxidation and reduction of the metal diminish its power of occluding hydrogen. From one sample they obtained first 150 volumes of hydrogen, then 50 volumes. Johnson, working with copper, noticed the same peculiarity, which is exhibited to a less

striking extent by the metal used in the following two series of analyses:

XXV. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XXVI. 2.7 grams of cobalt yielded 0.0029 gram of water, or 12.3 volumes of hydrogen.

XXVII. 2.7 grams of cobalt yielded 0.0025 gram of water, or 10.5 volumes of hydrogen.

XXVIII. 2.7 grams of cobalt yielded 0.0035 gram of water, or 14.8 volumes of hydrogen.

XXIX. 2.7 grams of cobalt yielded 0.0025 gram of water, or 10.5 volumes of hydrogen.

XXX. 2.7 grams of cobalt yielded 0.0018 gram of water, or 7.5 volumes of hydrogen.

XXXI. 2.2 grams of cobalt yielded 0.0020 gram of water, or 10.2 volumes of hydrogen.

XXXII. 2.2 grams of cobalt yielded 0.0012 gram of water, or 6.2 volumes of hydrogen.

XXXIII. 2.2 grams of cobalt yielded 0.0019 gram of water, or 9.9 volumes of hydrogen.

XXXIV. 2.2 gram of cobalt yielded 0.0012 gram of water, or 6.2 volumes of hydrogen.

During the above process the metal gradually sintered together, occupying apparently much less volume than at first. If the same metal is then heated to redness in hydrogen it sinters much more still and yields only traces of hydrogen.

XXXV. 5.5 grams of cobalt yielded 0.0016 gram of water, or 3.5 volumes of hydrogen.

XXXVI. 6.2 grams of cobalt yielded 0.0004 gram of water, or 0.7 volume of hydrogen.

XXXVII. 2.5 grams of cobalt yielded 0.0003 gram of water, or 1.2 volumes of hydrogen.

Even impure oxide, obtained by igniting commercial nitrate, when heated to a high temperature in hydrogen, occluded only traces of this gas.

XXXVIII. 1.8 grams of cobalt yielded 0.0004 gram of water, or 2.5 volumes of hydrogen.

Metal reduced from impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided ten-

dency to cling together. Pure metal reduced at high temperatures forms a hard solid mass. This sintering can be nothing more nor less than incipient fusion.[1] Where the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect.

From the results of the work just described several important conclusions can be drawn. Cobalt in the form of ingots, which present a minimum amount of surface, is known to occlude almost no hydrogen. On the other hand, cobalt reduced from the oxide at a low temperature and consequently in a very finely divided condition offers a maximum amount of surface, and occludes relatively large amounts of hydrogen. Electrolytic foil, which, although it possesses considerable porosity, still lies between the above two modifications in relative surface, falls between them also in the amount of hydrogen retained. Neither Neumann and Streintz nor Troost and Hautefeuille took any precautions to purify their cobalt from alkalies or silica. Their metal, kept from sintering together by the impurities and the low reduction temperature, was in the finest state of division; consequently it proved to be pyrophoric and to occlude maximum amounts of hydrogen, just as in Analysis VIII of this paper. That this property of spontaneous oxidation was not due to the hydrogen but to the large amount of surface presented to the air is shown by the fact that the metal used by Troost and Hautefeuille was still pyrophoric after it had been heated in a vacuum. The pure metal used in the work just described sintered considerably even at the lowest temperature at which reduction took place, and accordingly occluded much less hydrogen than the impure metal; while even approximately pure metal when heated to a high temperature sintered together to such an extent that a minimum surface was presented to the hydrogen and only traces of this gas were occluded.

The first inference is perfectly clear. The volume of occluded hydrogen depends upon the amount of surface pre-

[1] Compare Richards: This JOURNAL, 20, 725 (1898).

sented, which in the case of metals reduced from the oxide varies with the purity of the metal and the temperature of reduction.

Again, since at ordinary temperatures the occlusion of hydrogen progresses very slowly (Analyses XXII and XXIII), while at the temperature of reduction, 400°–500°, it amounted to an almost negligible quantity (Analyses XXIV and XXV), at some intermediate temperature the occlusion must progress at a maximum rate.

Thirdly, the time during which the metal is in contact with the hydrogen is an important factor in determining the quantity of this gas taken up.

Finally, the volatility of cobaltous bromide evidently allows the metal reduced from it to be deposited in a form more compact and coherent than that reduced from the oxide, since the presence of sodic bromide was found to have no perceptible effect upon the amount of occluded gas.

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The Occlusion of Hydrogen by Nickel.

The study of the occlusion of hydrogen was extended to the case of a few other metals. The behavior of nickel was found to be analogous to that of cobalt. According to Troost and Hautefeuille[1] nickel in the form of ingots retains only traces of hydrogen, metal reduced from the oxide occludes maximum amounts and is pyrophoric, while electrolytic foil occupies a position between the two. The amount of occluded gas, according to their results, was equal in quantity to that obtained from cobalt, 100 volumes in the case of metal reduced from the oxide. Raoult[2] states that very porous nickel, if used as the negative pole of a voltameter, takes up 165 volumes of hydrogen, the greater part of which is given off at ordinary temperatures in the air. These high results are contradicted by those of Neumann and Streintz,[3] who found about 17 volumes of gas in metal reduced from the oxide, and by those of Richards and Cushman,[4] who found only 8 volumes in the purest metal obtained from the same source.

The lesser values are supported by the following analyses performed with material kindly furnished by Dr. Cushman,

[1] Compt. rend., **80**, 788.
[2] Jahresb., 1869, 272.
[3] Monatsh. Chem., **12**, 642.
[4] Proc. Amer. Acad., **34**, 333.

and known to be free from every impurity. In Analyses I and II the nickel was subjected to combustion immediately after reduction. The oxide from Analysis I was reduced, and the resulting metal evolved no hydrogen in a vacuum, as was shown by the water yielded upon subsequent oxidation (Analyses III and IV). When heated in a vacuum the metal lost nearly all its occluded hydrogen (Analysis V). Like cobalt, nickel which had been heated to a high temperature during reduction sintered together and lost its power to occlude (Analysis VI). Finally, material reduced from the bromide occludes no hydrogen (Analysis VII), as has already been shown by Richards and Cushman.[1]

I. 5.7 gram of nickel yielded 0.0033 gram of water, or 5.7 volumes of hydrogen.

II. 4.0 grams of nickel yielded 0.0010 gram of water, or 2.1 volumes of hydrogen.

III. 5.7 grams of nickel yielded 0.0060 gram of water, or 10.7 volumes of hydrogen.

IV. 5.7 grams of nickel yielded 0.0057 gram of water, or 10.2 volumes of hydrogen.

V. 5.7 grams of nickel yielded 0.0017 gram of water, or 2.9 volumes of hydrogen.

VI. 6.0 grams of nickel yielded 0.0006 gram of water, or 1.0 volume of hydrogen.

VII. 1.5 grams of nickel yielded 0.0001 gram of water, or 0.7 volume of hydrogen.

Manifestly nickel is subject to the same influences as cobalt. The large amounts of hydrogen obtained by other experimenters can be explained by the fact that their material was very impure. Impure nickel and cobalt in the same state of minute subdivision apparently possess the property of retaining hydrogen to the same degree. Pure nickel, owing to its lower melting-point, should sinter more readily than pure cobalt. The lesser relative surface thus offered is probably the reason for the smaller amounts of occluded gas.

The Occlusion of Hydrogen by Copper.

The occlusion of hydrogen by copper has already been the subject of numerous researches which gave widely varying

[1] Proc. Amer. Acad., **34**, 333.

results.[1] One main fact stands out in all these investigations. Where the copper was known to be pure the occlusion was very slight, whatever the source of the copper.

Very pure cupric oxide, made by evaporation of a solution of electrolytic copper in pure nitric acid, and ignition of the residue, after reduction yielded a very small amount of water (Analyses I, II, III, and IV). In a vacuum at ordinary temperatures the hydrogen was retained (Analysis 5), but after ignition in a vacuum a negligible amount of water was found (Analysis VI).

I. 2.5 grams of copper yielded 0.0003 gram of water, or 1.5 volumes of hydrogen.

II. 5.1 grams of copper yielded 0.0009 gram of water, or 2.1 volumes of hydrogen.

III. 5.1 grams of copper yielded 0.0010 gram of water, or 2.3 volumes of hydrogen.

IV. 5.1 grams of copper yielded 0.0009 gram of water, or 2.1 volumes of hydrogen.

V. 5.1 grams of copper yielded 0.0008 gram of water, or 1.8 volumes of hydrogen.

VI. 5.1 grams of copper yielded 0.0003 gram of water, or 0.7 volume of hydrogen.

The Occlusion of Hydrogen by Silver.

Silver reduced from the oxide takes up minimum amounts of hydrogen, if any.

I. 2.5 grams of silver yielded 0.0001 gram of water, or 0.5 volume of hydrogen.

II. 2.5 grams of silver yielded 0.0005 gram of water, or 2.8 volumes of hydrogen.

III. 5.0 grams of silver yielded 0.0003 gram of water, or 0.8 volume of hydrogen.

This result is in accordance with the results of Graham,[2] whose silver wire occluded 0.2 its volume of the gas, while his metal obtained by reduction of the oxide yielded 0.9 its

[1] Graham: Jsb., 1866, 50; Thudichum and Hake: Jour. Chem. Soc., **33**, (2) 251, (1876); Johnson: Jour. Chem. Soc., **35**, 235; Neumann and Streintz: Monatsh. Chem., **12**, 642; Richards: Proc. Amer. Acad., **26**, 292; and others.

[2] Jsb., 1866, 51.

volume. Neumann and Streintz found no hydrogen in their silver reduced from the oxide.[1]

It is noteworthy that in all the work performed upon the occlusion of hydrogen by the four metals, cobalt, nickel, copper, and silver, when they were reduced from pure oxides at low temperatures, the magnitude of the occlusion varied with the fusion-points of the metals. Cobalt, whose melting-point is the highest, occludes by far the greatest volume of gas; while silver, which melts at the lowest temperature, occludes minimum quantities. The explanation of this peculiarity has already been mentioned. The sintering or fusing together of the metals is greater, the nearer the reduction temperature is to their melting-points; while the surface offered, which determines the amount of occlusion, diminishes with the amount of sintering. Since the melting-points of copper and silver are very near together, one would expect their power of occlusion to be very nearly the same, as is the case.

Pure ferric oxide is not reduced to any considerable extent by hydrogen at the low temperature employed in the case of the four preceding metals. When a temperature sufficiently high to produce reduction is employed, no appreciable amounts of hydrogen are occluded because of sintering of the metal. On account of this difficulty no work could be done with iron which would be comparable with that done with the other metals.

The question as to the formation of compounds of the metals with hydrogen, similar to "Hydrogenium," is not easily settled. On the one hand, the fact that the quantity of occluded gas varies with the surface presented seems to point to simple condensation on the surface as in the case of charcoal; on the other hand, the pertinacity with which the hydrogen is retained in a vacuum when cold is evidence in the other direction. For the present this point must needs remain undecided.

A word can be profitably said here in regard to the use of the terms "occlusion" and "adsorption." In its stricter sense the word "occlusion" should be confined to an intimate combination, such as that of palladium with hydrogen.

[1] Monatsh. Chem., 12, 642.

"Adsorption," on the other hand, refers to simple condensation or concentration in the immediate vicinity of a given surface. Owing to the doubt as to the nature of the process by which the hydrogen is retained by the metals considered, the question as to the designation of the process is necessarily unsettled, but Graham's word has been usually employed above.

In conclusion, I wish to express my thanks to Professor Theodore William Richards for much advice and encouragement given during the course of this work.

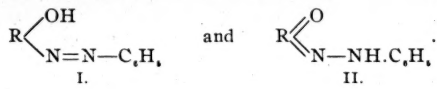
CAMBRIDGE, MASS., June 15, 1899.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE NATURE OF THE OXYAZO COMPOUNDS.

BY WILLIAM MCPHERSON.

The oxyazo compounds have been under investigation for the past fifteen years, especially because no decisive conclusion has been reached as to their constitution. Two general formulæ have been assigned to them; *viz.*,



I. and II.

According to the first of these, they are true oxyazo bodies; the second represents them as derivatives of quinones; *viz.*, quinonehydrazones. Goldschmidt, in consequence of results obtained with his students in the case of ortho- and paraoxyazo derivatives decided[1] that these compounds must all be regarded as monohydrazones of quinones or diketones. This conclusion, however, is not in accord with his own previous results obtained with phenyl isocyanate.[2] On the other hand, Jacobson,[3] Meldola,[4] Witt and Schmidt,[5] Noelting and Grandmougin,[6] working chiefly with alkylated substitution-products

[1] Goldschmidt and Brubacher: Ber. d. chem. Ges., **24**, 2300; Goldschmidt and Pollak: *Ibid.*, **25**, 1324.

[2] Goldschmidt and Rosell: *Ibid.*, **23**, 487.

[3] *Ibid.*, **25**, 992: **26**, 681; and **27**, 2700.

[4] J. Chem. Soc., **53**, 460; **55**, 114 and 603; **59**, 372-710; **63**, 923; **65**, 834.

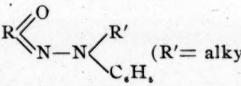
[5] Ber. d. chem. Ges., **25**, 1013.

[6] *Ibid.*, **24**, 1592.

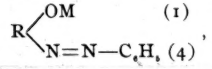
or in the ortho series, came to conclusions directly opposite to those reached by Goldschmidt.

The oxyazo compounds may conveniently be divided into two classes; namely, those belonging to the ortho series and those belonging to the para series. It does not of necessity follow that the compounds of the one series possess a constitution analogous to that of the other.

In order to attack this problem from an entirely new standpoint, I undertook, at the suggestion and under the direction of Dr. J. U. Nef, the study of the action of unsymmetrical alkylated and acylated derivatives of phenylhydrazine on various quinones, both of the ortho and the para series. The condensation-products thus obtained,

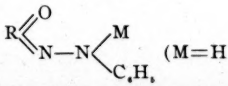

(R′= alkyl or acyl),

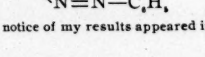
were compared with the free oxyazo compounds and the corresponding products obtained from these by direct alkylation and acylation.[1] The results are decisive; they prove that all paraoxyazo compounds, their salts as well as the acylated and alkylated substitution-products, possess the general formula


(1)
(4)
, (M=H, a metal, acyl or alkyl); *i. e.*,

all are true oxyazo compounds.

The work in the ortho series, while not so decisive nor so exhaustive, all points now to one conclusion; namely, that these compounds and their acylated substitution-products are monohydrazones of orthodiketones,

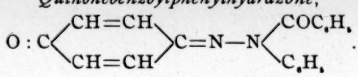

(M=H or acyl).

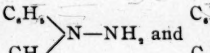
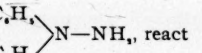
The alkylated substitution-products, on the other hand, are azo compounds,  .

[1] A preliminary notice of my results appeared in the Ber. d. chem. Ges., **28**, 2414.

I. The Action of α-Acylated Phenylhydrazines on Paraquinones.

Quinonebenzoylphenylhydrazone,



Benzoquinone and its homologues react with phenylhydrazine with evolution of nitrogen and formation of resinous products.[1] Since hydroxylamine[2] and its α-alkylated substitution-products[3] react in a normal manner with quinone, it seemed possible that a replacement of the imide hydrogen in phenylhydrazine by acyl or alkyl might give rise to products which would condense in a normal manner with paraquinones; whereas, it was found that α-methyl and α-benzylphenylhydrazine,  and  , react with benzo-, toluo-, and thymoquinone with formation of hydroquinone and tetrazones (see below); α-naphthoquinone reacts, just as with phenylhydrazine itself in a perfectly normal manner with these reagents. All these quinones, however, give normal condensation-products on treatment with α-acylated phenylhydrazines.

One and two-tenths grams of α-benzoylphenylhydrazine hydrochloride, made according to the directions of Widman,[4] were dissolved in 300 cc. of water containing a few drops of hydrochloric acid. To this was added a solution of 0.5 gram benzoquinone in 200 cc. of water. A yellow precipitate begins to separate out at once and, after two hours, the reaction is completed. Yield 1.3 grams (theory 1.4 grams). The substance was purified by recrystallizing twice from benzene, in which it readily dissolves while hot and from which it is deposited on cooling in yellow, flat needles or in prisms melting at 171°.

0.1870 gram substance gave 15.5 cc. nitrogen at 24.5° and 744.8 mm.

[1] Zincke: Ber. d. chem. Ges., **16**, 1563.
[2] Goldschmidt: *Ibid.*, **17**, 213.
[3] Bridge: Ann. Chem. (Liebig), **277**, 90, 95.
[4] Ber. d. chem. Ges., **26**, 945.

0.1961 gram substance gave 0.5410 gram CO_2, and 0.0900 gram H_2O.

	Calculated for $C_{19}H_{14}N_2O_2$.	Found.
C	75.49	75.22
H	4.63	5.10
N	9.29	9.15

Quinonebenzoylphenylhydrazone is very difficultly soluble in cold ether and alcohol. It separates out from hot alcohol in groups of crystals resembling sodium chloride; if the solution, however, is cooled very slowly, heavy, transparent, reddish-yellow crystals with numerous well-defined facets are obtained. The substance is readily soluble in chloroform and glacial acetic acid, moderately soluble in cold benzene, and insoluble in ligroin, and can therefore also be purified by crystallizing from a mixture of benzene and ligroin.

Behavior towards Reducing Agents.

Quinonebenzoylphenylhydrazone (1 gram) treated in cold acetic acid solution with zinc dust is split, in a few minutes, quantitatively into benzanilide and paramidophenol; on addition of water to the filtered solution, benzanilide separates out in plates (0.55 gram). These were purified by distillation and subsequent crystallization from alcohol. Yield, 0.3 gram of pure product melting at 161°.

0.2454 gram substance gave 16.1 cc. nitrogen at 26°.2 and 743.8 mm.

	Calculated for $C_{13}H_{11}NO$.	Found.
N	7.11	7.15

The presence of paramidophenol in the filtrate was established, after precipitating the zinc with hydrogen sulphide, by converting it into the hydrochloride and then by means of calcium hypochlorite[1] into quinonechlorimide; melting-point found, 85°.

This decomposition, which was also established in the case of the corresponding derivatives of toluo-, thymo-, and α-naphthoquinone, is entirely analogous to those observed by Goldschmidt[2] in the reduction of a whole series of acetyl and ben-

[1] Fogh: Ber. d. chem. Ges., **21**, 890.
[2] *Ibid.*, **24**, 2300, and **25**, 1324.

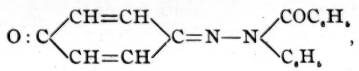
zoyl derivatives of orthooxyazo compounds both in the benzene as well as in the naphthalene series. This proves that the conclusions drawn by him from those results, *viz.*, that the acyl groups are bound to nitrogen and not to oxygen are entirely justifiable.

Behavior towards Phenylhydrazine.

Quinonebenzoylhydrazone reacts on addition of phenylhydrazine with such explosive violence that complete charring takes place. Even in dilute alcoholic or acetic acid solutions, decolorization, with decided evolution of heat and of nitrogen, takes place. This substance therefore behaves towards this reagent in a manner analogous to quinone and its homologues.

Comparison with Goldschmidt's so-called Quinonebenzoylphenylhydrazone.

The quinonebenzoylphenylhydrazone described above, which, from its method of synthesis and its properties, unquestionably possesses the constitution,



is *isomeric*, *not identical*, with the benzoyl derivative which can be obtained from paraoxyazobenzene by means of Baumann's reaction, or directly by heating it with benzoic anhydride. The benzoate of paraoxyazobenzene melts at 138° and crystallizes from alcohol, as was observed in a preparation made according to Tschirwinsky's directions,[1] in thin, voluminous, yellow plates or scales. Zinc and acetic acid convert it into the colorless dihydride described by Goldschmidt and Brubacher[2] (melting-point found, 172°.5). This compound is readily converted, as I have observed, by adding ferric chloride or mercuric oxide to its alcoholic solution, back again into the yellow benzoate of paraoxyazobenzene. Tschirwinsky's benzoate of paraoxyazobenzene is furthermore split in the cold by treatment with concentrated sulphuric acid or with alcoholic potash into benzoic acid and paraoxyazoben-

[1] Ber. d. chem. Ges., **6**, 561.
[2] *Ibid.*, **24**, 2302; and **25**, 1325.

zene. This compound must therefore possess the constitution, $C_6H_5CO-O-C_6H_3(CH=CH)_2-C-N=N.C_6H_5$, and not the isomeric formula given it by Goldschmidt and Brubacher; its dihydride, discovered by Goldschmidt and Brubacher, is therefore the corresponding hydrazo derivative,

$$C_6H_5CO-O-C_6H_4-NH-NH-C_6H_5.$$

Goldschmidt has indeed given all the acetyl and benzoyl derivatives of paraoxyazo compounds the quinonehydrazone formula, *i. e.*, he assumes that the acyl group introduced is bound to nitrogen and not to oxygen. He was never able, however, to bring forward decisive experimental proof for this assumption in the case of paraoxyazo compounds. He never succeeded, for example in establishing a splitting of these compounds into acetanilide or benzanilide, respectively, as he had done in the case of the orthooxyazo compounds. His conclusions were therefore based chiefly on the conviction that all oxyazo compounds, the ortho as well as the para, must possess an analogous constitution, a conclusion which, as is now evident, was not justifiable.

A comparison of the quinone derivatives obtained by means of α-benzoylphenylhydrazine, from toluo-, thymo-, and α-naphthoquinone, with the corresponding benzoates from benzeneazoorthocresol, benzeneazothymol, benzeneazo-α-naphthol, in like manner establishes that the products are isomeric and not identical (see below).

Behavior of Quinonebenzoylphenylhydrazone towards Saponifying Agents.

The behavior of the actual quinonebenzoylphenylhydrazone towards concentrated sulphuric acid and alcoholic potash is very interesting. It is split, after standing in the cold, quantitatively into benzoic acid and paraoxyazobenzene. The same result is obtained on adding dilute hydrochloric acid to a hot alcoholic solution of the substance. The experiment was carried out in every case with 0.5 gram of material and the paraoxyazobenzene obtained very carefully compared with

a preparation made in the ordinary manner. All products melted at 152° and crystallized from benzene in peculiar flat crystals grouped together. Furthermore, they were all converted by means of Baumann's reaction into the ordinary benzoylated paraoxyazobenzene,

$$C_6H_5CO—O—C_6H_4N=NC_6H_5,$$

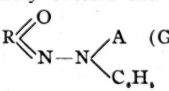
of Tschirwinsky (melting-point observed, 138°, thin plates).

These experiments prove that, on saponification, quinonebenzoylphenylhydrazone, as well as its isomer, the benzoate of paraoxyazobenzene, give one and the same product; *viz.*, paraoxyazobenzene, $OH—C_6H_4N_2—C_6H_5$. That this substance possesses a constitution represented by its name, that it is not quinonephenylhydrazone,

$$O=C_6H_4=N—NH—C_6H_5,$$

or a tautomeric compound, the following facts establish beyond a reasonable doubt:

1. Paraoxyazobenzene, by direct acylation of alkylation, gives acyl as well as alkyl derivatives, which unquestionably and exclusively contain the acyl as well as the alkyl group bound to oxygen, $C_6H_5—N_2—C_6H_4—OM$ (M=acyl or alkyl). This is proved in the case of the acyl derivatives by the experiments described in this paper, and in the case of the alkyl derivatives by the experiments of Jacobson.[1]

2. The orthooxyazo derivatives by direct acylation give products which as unquestionably contain the acyl group bound exclusively to nitrogen,  (Goldschmidt and others).

3. The free paraoxyazo compounds do not react, as I have observed, in the case of paraoxyazobenzene and others, with phenylhydrazine, either directly or in alcoholic solution, even if heated to 100°, whereas all paraquinonebenzoylphenylhydrazone derivatives, like benzoquinone itself, react with this reagent with explosive violence. Were oxyazobenzene identical with quinonehydrazone, $O : C_6H_4=N—NH—C_6H_5$, it is

[1] *Loc. cit.*

difficult to understand its indifference to phenylhydrazine as compared with the intense activity of its nitrogen-acylated derivatives.

4. The paraoxyazo compounds are all freely soluble in dilute caustic alkalies and in some cases even in dilute alkaline carbonates; in marked contrast is the behavior of the orthooxyazo compounds of the naphthalene series which are unquestionably quinonehydrazones. Thus benzeneazo-β-naphthol, $C_{10}H_6{=}O\ (\beta)$ / $N.NH.C_6H_5\ (\alpha)$, and β-naphthoquinone-phenylhydrazone, $C_{10}H_6{=}O\ (\alpha)$ / $N.NH.C_6H_5\ (\beta)$, are insoluble in and not affected by most concentrated caustic alkalies.[1] The isomeric para compound, $C_{10}H_6{<}OH\ (\alpha)$ / $N_2C_6H_5\ (\alpha')$, which remarkably enough is formed when α-naphthoquinone is treated with phenylhydrazine,[2] is, on the other hand, easily soluble even in alkaline carbonates. These noteworthy differences become self-evident if the paraoxyazo compounds are regarded as phenols.

5. A study of the physical properties of the free paraoxyazo compounds, carried out after my preliminary experiments, has led Auwers and Orton[3] to results entirely in accord with those obtained by chemical methods.

Quinoneacetylphenylhydrazone.

$$O{=}C\begin{cases}CH{=}CH\\CH{=}CH\end{cases}C{=}N{-}N\begin{cases}COCH_3\\C_6H_5\end{cases}.$$

The α-acetylphenylhydrazine used to prepare this compound was made from acetylformazylhydride according to Peckmann's directions[4] and also by Widman's method.[5] The latter method is more convenient. 0.5 gram of α-acetyl-

[1] Liebermann: Ber. d. chem. Ges., **16**, 2858; Zincke and Bindewald: *Ibid.*, **17**, 3031.

[2] Zincke and Bindewald: *Ibid.*, **17**, 3026.

[3] Zeit. phys. Chem., **21**, 356.

[4] V. Peckmann: Ber. d. chem. Ges., **27**, 1695.

[5] Widman: *Ibid.*, **27**, 2964.

phenylhydrazine hydrochloride was dissolved in 25 cc. of water and acidified with a few drops of hydrochloric acid; to this was added a solution of 0.4 gram benzoquinone in 30 cc. of 10 per cent alcohol. Yellow crystals soon began to separate out; after half an hour these were filtered off and dried (yield, 0.58 gram). Recrystallized from a mixture of benzene and ligroin, the substance was obtained in flat, yellow needles melting at 118°.

0.2238 gram substance gave 24.2 cc. nitrogen at 25° and 743.3 mm.

0.1794 gram substance gave 0.4587 gram CO_2, and 0.0800 gram H_2O.

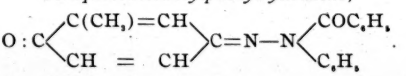
	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
C	70.00	69.73
H	5.00	4.95
N	11.66	11.86

The substance is very soluble in benzene and chloroform, less so in alcohol and ether. It reacts violently with phenylhydrazine and is converted by alcoholic potash or concentrated sulphuric acid into paraoxyazobenzene. It is *isomeric, not identical*, with the acetate or paraoxyazobenzene,

$$C_6H_5N_2—C_6H_4—O—CO—CH_3,$$

which has been prepared by Wallach and Kiepenhauer;[1] the latter substance, prepared according to their directions, was found to crystallize from benzene-ligroin in plates melting at 89°.5, instead of 84°–85°, as given by these observers. Alcoholic potash splits it into paraoxyazobenzene and acetic acid.

Toluquinonebenzoylphenylhydrazone,



Toluquinone, 0.4 gram, dissolved in 120 cc. of dilute alcohol, was added to a solution of 1 gram α-benzoylphenylhydrazine sulphate in 180 cc. of 10 per cent alcohol. A yellow precipitate began to separate out at once. After two hours this was filtered off and recrystallized three times from benzene.

[1] Wallach and Kiepenhauer: Ber d. chem. Ges., 14, 2617.

0.1892 gram substance gave 0.5181 gram CO_2, and 0.0921 gram H_2O.

0.1732 gram substance gave 13.9 cc. nitrogen at 23°.5 and 745 mm.

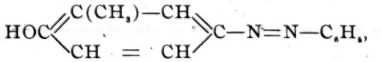
	Calculated for $C_{20}H_{18}N_2O_2$.	Found.
C	75.94	75.89
H	5.06	5.50
N	8.86	8.90

Toluquinonebenzoylphenylhydrazone is very soluble in ether and chloroform, moderately so in benzene, alcohol, and acetone. It separates from benzene or from benzene-ligroin in small, square, yellow tablets, melting at 151°. From alcohol it is deposited in red tablets or in yellow, feathery crystals. Treated with zinc dust and acetic acid, the hydrazone (0.5 gram) is split into benzanilide, melting-point 151°. A nitrogen determination gave the following result:

0.2132 gram substance gave 14.3 cc. nitrogen at 22° and 746 mm.

	Calculated for $C_{13}H_{11}NO$.	Found.
N	7.11	7.59

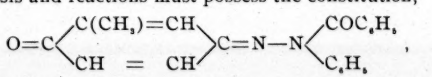
That the hydrazone has the constitution above given is proved by its method of synthesis and by its conversion, on treatment with alcoholic potash, into benzeneazoorthocresol,



obtained in yellow plates melting at 128°–130°.

Comparison with Goldschmidt's So-called Toluquinonebenzoylphenylhydrazone.

The compound described above, which from its method of synthesis and reactions must possess the constitution,



is *isomeric, not identical,* with the benzoate of benzeneazoorthocresol, first described by Noelting and Kohn,[1] and afterwards,

[1] Liebermann and Kostanecki: Ber. d. chem. Ges., 17, 131, 879: Cf. Noelting and Kohn: *Ibid.*, 17, 366.

(as well as the corresponding acetate), regarded by Goldschmidt[1] as being a quinone derivative. The latter compound melts at 110°, and is split by alcoholic potash into benzeneazoorthocresol. Its dihydride melts at 142°, and is readily oxidized to the original benzoyl derivative by means of ferric chloride. It is evident therefore that the formula given by Goldschmidt to the acylated derivatives of benzeneazoorthocresol and their dihydrides must be changed to

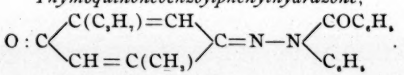
$$AO—C_6H_3(CH_3)—N=N—C_6H_5$$

and

$$AO—C_6H_3(CH_3)—NH—NH—C_6H_5,$$

respectively.

Thymoquinonebenzoylphenylhydrazone,



Four grams α-benzoylphenylhydrazine sulphate, dissolved in 350 cc. of 14 per cent alcohol, were added to a solution of 2 grams of thymoquinone in 300 cc. of 33 per cent alcohol. The mixture was heated until the quinone, partially precipitated, had redissolved and then allowed to stand twenty-four hours, when the yellow precipitate was filtered off. On examination this was found to be a mixture of two products, one yellow, the other colorless.[2] Their separation was accom-

[1] Ber. d. chem. Ges., **25**, 1331.

[2] In the interaction between acylated hydrazines and quinones, it was generally found best to add a concentrated alcoholic solution of the quinone to an aqueous solution of the hydrazine salt whereby the quinone is at first precipitated in a finely divided condition. It was found, however, that if the reaction in the above instance was carried out in this way, the principal product was a crystalline substance, which is best purified by washing with small quantities of cold benzene, and then dissolving the insoluble part in hot benzene with addition of animal charcoal. On filtering and cooling, snow-white needles melting at 155° were obtained.

0.2030 gram substance gave 21 cc. nitrogen at 20°.5 and 736.4 mm.
0.1749 gram substance gave 17.7 cc. nitrogen at 19° and 736 mm.
0.1705 gram substance gave 0.4437 gram CO_2, and 0.0853 gram H_2O.
0.1730 gram substance gave 0.4512 gram CO_2, and 0.0868 gram H_2O.

	Calculated for $C_{18}H_{14}N_2O_2$.	Found.	
C	70.86	70.96	71.12
H	5.51	5.56	5.56
N	11.02	11.40	11.31

Small amounts of a colorless substance were also obtained in the case of toluo- and α-naphthoquinone. Inasmuch as these seemed to have no particular bearing on the subject under investigation, no further study of them has yet been made, although it is my intention to examine them later.

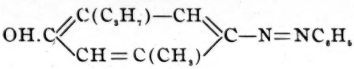
plished by repeated treatment with small amounts of cold benzene which dissolves only the yellow product; recrystallized from benzene-ligroin, the last-named substance was obtained in yellow plates melting at 132°.

0.1746 gram substance gave 13 cc. nitrogen at 23° and 745 mm.

0.1739 gram substance gave 0.4892 gram CO_2, and 0.1003 gram H_2O.

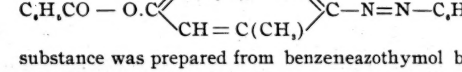
	Calculated for $C_{23}H_{22}N_2O_2$.	Found.
C	77.09	76.71
H	6.14	6.41
N	7.82	8.20

Thymoquinonebenzoylhydrazone is very soluble in chloroform and benzene, moderately so in alcohol, and with difficulty in ether. Reduced with zinc dust and acetic acid in the cold, it is split into benzanilide, melting-point 163°. Saponified by means of alcoholic potash, it gives benzoic acid and benzeneazothymol,[1] melting-point 93°.



This, together with the method of synthesis, proves the constitution of the quinonehydrazone to be that given above.

Benzoate of Benzeneazothymol,



— This substance was prepared from benzeneazothymol by means of Baumann's reaction, in order to compare it with the isomeric quinone derivative just described. Recrystallized twice from hot alcohol, it was obtained in reddish-yellow needles melting at 115°. It is consequently *isomeric*, and *not identical*, with the product in question.

0.2195 gram substance gave 16.2 cc. nitrogen at 22° and 740 mm.

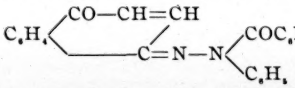
0.2081 gram substance gave 0.5881 gram CO_2, and 0.1151 gram H_2O.

[1] Mazzari and Passetto: Gazz. chim. ital., **15**, 53.

	Calculated for $C_{33}H_{32}N_2O_2$.	Found.
C	77.09	77.05
H	6.14	6.15
N	7.82	8.18

The benzoate of benzeneazothymol is very soluble in hot benzene and chloroform, moderately so in ether and ligroin. It is converted by means of alcoholic potash into benzoic acid and benzeneazothymol, whose melting-point was found to be 93° and not 85°–90°, as given by Mazzari and Possetto.

α-Naphthoquinonebenzoylphenylhydrazone,



Two grams of α-naphthoquinone, dissolved in a small amount of alcohol, were poured into a liter of water, and thereupon an excess (5 grams) of α-benzoylphenylhydrazine sulphate, dissolved in 200 cc. of 40 per cent alcohol, added. The mixture was heated to 70°–80° and then allowed to stand for twenty-four hours. The crude product, 4.5 grams, was purified by repeated crystallization from benzene-ligroin and obtained in yellow silky needles, melting at 161°.5.

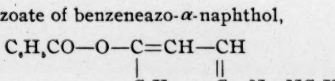
0.1848 gram substance gave 0.5312 gram CO_2, and 0.0814 gram H_2O.

0.2641 gram substance gave 18.7 cc. nitrogen at 25° and 745.3 mm.

	Calculated for $C_{33}H_{24}N_2O_2$.	Found.
C	78.40	78.35
H	4.54	4.90
N	7.95	7.78

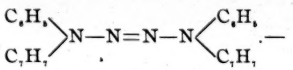
The substance is very soluble in benzene; it dissolves less readily in ether and alcohol, and is insoluble in ligroin. Reduced with zinc dust and acetic acid, it is split into benzanilide. Alcoholic potash converts it into benzeneazo-α-naphthol, melting-point 205°, from which was obtained the benzoate, melting-point 121°.5.

The benzoate of benzeneazo-α-naphthol,



has been prepared by Meldola;[1] it is *isomeric, not identical*, with the compound just described, and consequently must have its benzoyl group bound to oxygen. The formulæ given by Goldschmidt and Brubacher[2] to the acylated derivatives of α-naphthoquinonehydrazone or benzeneazo-α-naphthol and the corresponding dihydrides are therefore incorrect. The benzoate derivative can easily be prepared by Baumann's reaction, using barium hydroxide instead of sodium hydroxide. It is very slightly soluble in alcohol, ether, and hot ligroin, and always separates out in yellow needles melting at 121°.5. The two modifications described by Meldola were never observed.

II. Action of α-Alkylated Phenylhydrazines on Paraquinones.

Diphenyldibenzyltetrazone,  .—When benzoquinone and α-methylphenylhydrazine hydrochloride are brought together in dilute aqueous solution, an evolution of nitrogen is observed, and dimethyldiphenyltetrazone (melting-point 133°) separates out in leaflets (50 per cent of the calculated quantity).

Equimolecular proportions of benzoquinone and α-benzylphenylhydrazine sulphate (made by Widman's method) react at once in dilute aqueous solution; a strong odor of benzaldehyde is noticed and a bright yellow precipitate appears. After three hours' standing this was filtered off and purified by treatment in benzene solution with animal charcoal and repeated crystallization from benzene-ligroin. Colorless rhombohedra, melting with decomposition at 145°, were obtained. Philips[3] mentions a substance melting at 109°, obtained by him from benzylphenylhydrazine by oxidation with

[1] J. Chem. Soc., **55**, 606.
[2] Ber. d. chem. Ges., **24**, 2313-14.
[3] *Ibid.*, **20**, 2487.

mercuric oxide; no analysis is given and it is evident that the product was very impure.

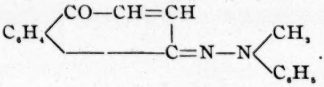
0.2040 gram substance gave 26.7 cc. nitrogen at 23° and 749.3 mm.

0.1648 gram substance gave 0.4822 gram CO_2, and 0.0895 gram H_2O.

	Calculated for $C_{16}H_{14}N_4$.	Found.
C	79.59	79.79
H	6.12	6.03
N	14.29	14.61

The action of α-alkylated phenylhydrazines on tolu- and thymoquinone is similar to that described in the case of benzoquinone.

α-Naphthoquinonemethylphenylhydrazone,



A solution of 5 grams of α-naphthoquinone in a small amount of alcohol was poured into a liter of water. To this was added a solution of 6 grams of α-methylphenylhydrazine sulphate in 200 cc. of 10 per cent alcohol. A slight evolution of gas was observed, and, after standing over night, a dark-red, very bulky precipitate appeared. The crude product, 6.2 grams, was purified by crystallizing three times from benzene-ligroin, and thus obtained in long, flat, amethyst-colored crystals which assume a metallic luster when powdered, and melt at 118°.5.

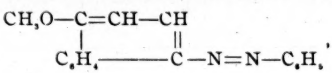
0.2398 gram substance gave 22.5 cc. nitrogen at 24° and 745 mm.

0.1550 gram substance gave 0.4404 gram CO_2, and 0.0765 gram H_2O.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.48
H	5.34	5.48
N	10.68	10.40

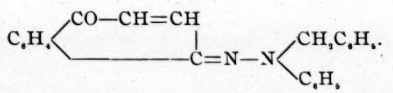
The quinonehydrazone is very soluble in benzene and chloroform, moderately so in alcohol and ether, and insoluble in

cold ligroin. The substance is *isomeric, not identical*, with the methyl ether obtained from benzeneazo-α-naphthol;[1] this compound, made according to the directions of Zincke and Bindewald, was separated from resinous products by means of cold ligroin, brown needles melting at 82°–83°. The latter compound must therefore possess the formula,



as has already been made probable by the experiments of Witt and Schmidt,[2] and others.

α-Naphthoquinonebenzylphenylhydrazone,



α-Naphthoquinone, 0.5 gram, dissolved in a small amount of alcohol, was poured into 300 cc. of water, and then a solution of 1 gram of α-benzylphenylhydrazine sulphate in 50 cc. of 10 per cent alcohol, which had been acidified with 2 cc. of strong sulphuric acid, was added. After standing over night, a tarry, dichroic mass had separated out which readily solidified when scratched. The product was obtained pure only after eight crystallizations from benzene-ligroin. It is very soluble in chloroform and benzene, sparingly soluble in alcohol and ether, and was obtained from benzene-ligroin in yellow, dichroic, flat needles, melting at 136°.

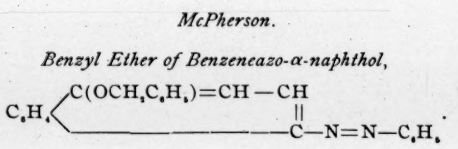
0.1998 gram substance gave 15.5 cc. nitrogen at 24° and 741.5 mm.

0.1876 gram substance gave 0.5632 gram CO_2, and 0.0962 gram H_2O.

	Calculated for $C_{23}H_{18}N_2O$.	Found.
C	81.65	81.80
H	5.30	5.55
N	8.26	8.52

[1] Zincke and Bindewald: Ber. d. chem. Ges., **17**, 3026.
[2] *Ibid.*, **25**, 1013

Benzyl Ether of Benzeneazo-α-naphthol,



An alcoholic solution of 5 grams benzeneazo-α-naphthol, prepared from α-naphthol and phenyldiazonium nitrate, was treated with 1.6 grams caustic soda and 5 grams benzyl chloride. The reaction was complete after five hours' heating. The product obtained was separated from some tar by recrystallizing from benzene-ligroin. It is very soluble in benzene but insoluble in ligroin. It consists of ruby-red, monoclinic crystals, which melt at 102°. When powdered, these become yellow.

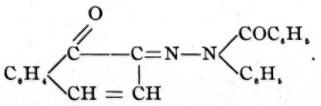
0.1962 gram substance gave 15.4 cc. nitrogen at 28°.5 and 748.8 mm.

0.2000 gram substance gave 0.6020 gram CO_2, and 0.1020 gram H_2O.

	Calculated for $C_{23}H_{18}N_2O$.	Found.
C	81.65	82.08
H	5.30	5.66
N	8.26	8.51

III. The Action of α-Alkylated and of α-Acylated Phenylhydrazines on β-Naphthoquinonehydrazone.

The Benzoate of β-Naphthoquinonephenylhydrazone is Identical with β-Naphthoquinonebenzoylphenylhydrazone,



The benzoyl derivative of β-naphthoquinonehydrazone can readily be prepared by adding benzoyl chloride to an alcoholic solution of the hydrazone, containing 1 molecule of sodium ethylate. Reaction takes place in the cold. The benzoate formed was purified by recrystallization from ben-

zene-ligroin. It forms yellow needles, melting at 191°, sparingly soluble even in hot alcohol, and fairly soluble in benzene.

0.2524 gram substance gave 18.6 cc. nitrogen at 24°.5 and 740.3 mm.

0.2080 gram substance gave 0.5983 gram CO_2, and 0.0904 gram H_2O.

	Calculated for $C_{22}H_{16}N_2O_3$.	Found.
C	78.40	78.44
H	4.54	4.83
N	7.95	8.07

The substance is readily split into its components, benzoic acid and β-naphthoquinonehydrazone, melting-point 138°, by treatment either with alcoholic potash or with concentrated sulphuric acid.

It can also be prepared from the hydrazone by heating with benzoic anhydride to 150° for five hours.

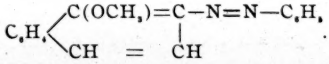
The corresponding acetate of β-naphthoquinonehydrazone has been prepared by Meldola[1] by means of acetic anhydride. This compound gives, according to Meldola, acetanilide on reduction with zinc dust and acetic acid. It can be obtained quantitatively, as I have found, by heating 5 grams of the hydrazone with 50 grams acetic anhydride and 20 grams fused sodium acetate for six hours at 100°.

That the benzoate of β-naphthoquinonehydrazone has the benzoyl group bound to nitrogen, is proved by its synthesis from β-naphthoquinone and α-benzoylphenylhydrazine sulphate. When these reagents are brought together in a dilute alcoholic solution, in a manner analogous to other cases described in this paper, a reaction takes place at once, even at 0°, with separation of a yellow precipitate. This product is so unstable that all attempts to purify it failed ; after filtration it is rapidly converted into a tarry mass. If the reaction is effected at higher temperatures, however, a normal condensation results. Two grams of the sulphate were dissolved in 180 cc. of 20 per cent. alcohol, and heated to boiling. As soon

[1] J. Chem. Soc., 65, 839.

as the air is expelled from the flask, a solution of 1 gram of β-naphthoquinone in 50 cc. of alcohol, was slowly added, and the boiling continued for twenty minutes. A bright-yellow precipitate separates out which gradually becomes tarry; on decanting and washing with hot alcohol, the impurities dissolve and leave a yellow crystalline residue, which, after recrystallization from benzene-ligroin, was obtained in yellow needles, melting at 191°, and identical in all their properties with the benzoate of β-naphthoquinonehydrazone just described.

Methyl Ether of β-Benzeneazo-α-naphthol,



The experiments of Meldola and of Noelting and Grandmougin[1] with β-naphthoquinonehydrazone, have already made it highly probable that the ethers obtained from this compound, by means of alkalies and alkyl haloids, contain the alkyl group bound to oxygen. The following experiments confirm these conclusions.

Two grams β-naphthoquinonehydrazone and 3 grams of methyl iodide were added to an alcoholic solution containing sodium methylate (from 0.5 gram sodium), and the mixture was heated to boiling for five hours. The methyl ether was precipitated by adding water and recrystallized several times from alcohol. It forms reddish-yellow plates readily soluble in benzene and hot alcohol, melting at 95°.

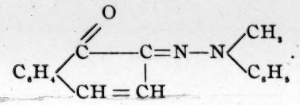
0.2234 gram substance gave 21.4 cc. nitrogen at 23° and 740 mm.

0.1622 gram substance gave 0.4609 gram CO_2, and 0.0753 gram H_2O.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.49
H	5.34	5.15
N	10.68	10.47

[1] Meldola: J. Chem. Soc., **65**, 834; Cf. also Noelting and Grandmougin: Ber. d. chem. Ges., **24**, 1592.

β-Naphthoquinonemethylphenylhydrazone,



Four grams of α-methylphenylhydrazine sulphate were dissolved in 500 cc. of water, containing 50 cc. of glacial acetic acid, and the mixture heated to 70°–80°. Thereto were slowly added 3 grams of β-naphthoquinone, dissolved in a small amount of alcohol, and the temperature kept at 80° for two hours. On cooling, the condensation-product was filtered off and recrystallized, after treatment with animal charcoal, from benzene-ligroin. It formed yellow nodules, melting at 134.5°, very soluble in benzene, and sparingly soluble in hot alcohol, from which, on cooling, needle-shaped crystals are obtained. The yield is small, not more than 2 per cent.

0.1834 gram substance gave 17.2 cc. nitrogen at 22° and 742 mm.

0.1632 gram substance gave 0.4644 gram CO_2, and 0.0797 gram H_2O.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.60
H	5.34	5.42
N	10.68	10.41

From the facts presented in this paper, and from previous experiments by Goldschmidt, Meldola, and others, it follows that β-naphthoquinonehydrazone is a quinone derivative; it gives by direct acylation, or by treatment with benzoyl chloride and sodium ethylate, acylated derivatives in which the acyl group is unquestionably and exclusively bound to nitrogen. With alkyl iodides and alkalies, on the other hand, it is converted into alkyl ethers, in which the alkyl group is undoubtedly and exclusively bound to oxygen. It is highly probable from facts recorded in the literature that all ortho-oxyazo compounds show a similar deportment on acylation and alkylation.

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING-POINT.[1]

By Garnett Ryland.

Introduction.

In the course of an investigation undertaken for another purpose a mixture of methyl alcohol and benzene was subjected to a fractional distillation, when it was observed that the larger part boiled like a homogeneous liquid at 57°–58°, and could not be separated by repeated distillation with a Hempel tube. By making trial mixtures it was found that, mixed in certain definite proportions, methyl alcohol and benzene will boil to the last drop at 57°–57°.5, under atmospheric pressure. If there is present an excess of either of the constituents, the constant boiling mixture and this excess are separated by fractional distillation. As roughly determined, the proper ratio seemed approximately $3CH_4O : 2C_6H_6$ (38.1 parts of alcohol to 61.9 parts of benzene, by weight).

On examination of the literature no such observation of this mixture could be found, though several similar phenomena are on record.

Historical Sketch.

1. H. E. Roscoe[2] investigated certain aqueous acids of constant boiling-point, which had been regarded as definite hydrates, and found that the proportions of water and acid were not those required by any simple molecular ratio, nor did the composition remain the same when the pressure varied.

Aqueous nitric acid, when distilled under a pressure of 735 mm., always gave a residue which boiled at 120°.5, and contained 68 per cent of pure acid. Distilled under 75 mm.

[1] From the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898. The investigation was undertaken at the suggestion of Professor Remsen, and carried on under his supervision.

[2] "On the Composition of Aqueous Acids of Constant Boiling-point." J. Chem. Soc., **13**, 146 (1861), and **15**, 270 (1862).

pressure, the per cent of pure acid was 66.7 ; and under 1260 mm. it became 68.8.

Aqueous solutions of hydrochloric, hydrobromic, and hydriodic acid gave similar phenomena, only in these cases the per cent of acid increased as temperature and pressure decreased. Hydrofluoric acid resembled nitric acid in all respects.

Aqueous formic acid containing 77.5 per cent of pure acid (boiling-point 101°.1), boiled at the fixed temperature of 107°.1, under 760 mm. pressure, the proportion of acid increasing with the pressure.

Aqueous perchloric acid[1] gave a residue which boiled constantly at 203°, under atmospheric pressure, and contained 71.6 per cent pure acid.

2. Alexander Bauer[2] found that a mixture of ethylene bromide (boiling-point 129°) and propylene bromide (boiling-point 141°) in equivalent amounts, distilled at 134°, and could not be separated by fractionation.

3. J. A. Wanklyn[3] called attention to the fact that in the distillation of a mixture of liquids the proportions in which the constituents pass over depend not merely on their relative quantity and on their respective vapor-tensions at the temperature of ebullition, but also upon their mutual adhesion and on the density of their vapors.

On distilling a mixture of 18 grams of methyl alcohol (boiling-point 66°) and 17 grams of ethyl iodide (boiling-point 72°), the first third of the distillate contained a greater amount of the less volatile than of the more volatile liquid.

4. Berthelot[4] stated that a mixture of 91 parts carbon disulphide (boiling-point 48°) and 9 parts alcohol (boiling-point 78°), by weight, boils at 43°–44°, remaining at this temperature from the beginning until the end of the distillation. A mixture of this composition is separated by fractional distillation from an excess of either of its components.

1 "On Perchloric Acid and Its Hydrates." Proc. Roy. Soc., **11**, 493 (1862).

2 "Ueber eine merkwürdige Erscheinung bei der Destillation eines Gemenges von Bromäthylen und Brompropylen." Ann. Supp.-Band, I (1861), p. 250.

3 "Ueber die Destillation von Gemischen ; ein Beitrag zur Theorie der fractionirten Destillation." Ann. Chem. (Liebig), **28**, 328 (1863).

4 "Sur la Distillation des Liquides melangés." Ann. chim. phys [4], **1**, 384 (1864).

He found the explanation of this phenomenon in essentially physical ideas. If a mixture of two liquids which do not exert any reciprocal action is boiled, both will be volatilized at that temperature at which their united vapor-tensions equal the atmospheric pressure, and in the same ratio by weight as that of the products of their actual vapor-tensions by their vapor-densities respectively. So if the carbon disulphide and alcohol preserved their theoretical vapor-tensions, they would be distilled at about 40° in the proportions of 88.5 parts of carbon disulphide and 11.5 parts of alcohol. But the two liquids exert influence upon each other, as is shown by their mutual solution and by the diminution of the sum of the tensions of their vapors. This influence tends to diminish the individual vapor-tension of each of the liquids, following an unknown law.

5. Ed. Linnemann[1] records three hydrates of isopropyl alcohol (boiling-point 83°–84°, 739 mm.); $3C_3H_8O + 2H_2O$, formed when aqueous propyl alcohol is distilled on the water-bath, boils at 78°–80° (738 mm.), specific gravity 0.832, at 15°; $2C_3H_8O + H_2O$, formed by dehydration with potassium carbonate, boils at 80°; $3C_3H_8O + H_2O$, formed by distilling from anhydrous copper sulphate, boils at 81°, specific gravity 0.800.

6. T. E. Thorp[2] found that a mixture of 1 part methyl alcohol and 3.6 parts carbon tetrachloride boils like a homogeneous liquid about 10° lower than methyl alcohol, the more volatile of the two liquids. Calculation shows that this ratio is almost identical with that obtained by multiplying the vapor-tensions of the two liquids at the temperature of the boiling-point (55.7°) by their respective vapor-densities.

7. D. Konowalow[3] investigated the known mixture of propyl alcohol (boiling-point 97°.4) and water in the ratio of about 77 : 23 parts, which boils at 85°–85°.5. To this composition corresponded the maximum of the curve, whose abscissæ are percentage quantities and ordinates pressures, rep-

[1] "Untersuchung über die Beziehungen des Isopropyl Alcohols zum Propyl Glycol und zum Glycerin." Ann. Chem. (Liebig), **136**, 40 (1865).

[2] "A Contribution to the Theory of Fractional Distillation." J. Chem. Soc., **35**, 544 (1879).

[3] "Ueber die Dampfspannungen der Flüssigkeitsgemische." Wied. Ann., **14**, 34 (1881).

resenting the vapor-tension of the mixture at a specific temperature.

He found also that a 25 per cent solution of butyric acid (boiling-point 163°) in water boiled constantly at 99°.5. Both of these mixtures change their respective proportions on change of the pressure and temperature of distillation.

8. Ramsay and Young[1] agreed with Konowalow that the mixture of propyl alcohol and water, thought by Chancel to be $C_3H_8O+H_2O$, which distils to the last drop at 87°.5 (738 mm.), is not a definite hydrate. The normal composition of the mixture (71.46 per cent alcohol to 28.54 per cent water) varied with the pressure under which it was distilled.

Apparatus for Distillation under Reduced Pressure.

Mixtures of methyl alcohol and benzene were distilled under different pressures, and the relative amounts of the two liquids contained in the constant boiling portion of the distillates were determined.

The apparatus used to effect fractional distillation, under reduced pressure, was arranged as follows :[2]

A 250 cc. separatory funnel was used as a receiver. This was closed with a two-hole rubber stopper, through which passed the adapter and a branched tube, the latter connecting with the manometer, the exhaust, and the pressure regulator. The last was a glass tube about 800 mm. in length and 20 mm. in diameter, filled to the necessary height with mercury, and closed at the top with a two-hole rubber stopper through which passed a short and a long piece of small glass tubing. The first connected with the receiver and the latter extended below the surface of the mercury a distance corresponding to the desired diminution of pressure. By this means the pressure could easily be kept constant within 10 mm. without interrupting the course of distillation. Successive fractions were drawn off from the funnel into an exhausted receiver, through whose stopper the stem of the funnel passed.

The liquid was distilled from a bulb provided with an addi-

[1] "Note on the Mixture of Propyl Alcohol and Water." Abs. Proc. Chem. Soc., 1888-1889, p. 101.

[2] My thanks are due to Dr. E. E. Reid, of this laboratory, for his kind assistance in designing and constructing this apparatus.

tional side tube, connected by rubber and a pinch-cock with a small funnel, into which successive fractions were poured. With caution these could be introduced without diminishing the exhaustion.

Methyl Alcohol and Benzene.

Method of Analysis.—The distillates were analyzed by the following method:

30–40 cc. of the fraction boiling at a constant temperature were measured off into a burette and a definite proportion of water added. It was found that when alcohol constituted 30–40 per cent of the distillate the water added should be one-third of the volume of the sample. The burette was closed, shaken vigorously, and allowed to stand until the liquid within separated into two sharply divided layers of benzene and aqueous alcoholic solution. The volume of benzene could then be read off and its volume ratio to the alcohol converted into the weight ratio by determining the specific gravity of each liquid.[1]

A series of 6 test determinations of known mixtures gave the following results for the per cent of benzene by volume:

	Per cent of benzene.					
	I.	II.	III.	IV.	V.	VI.
Calculated	58.8	59.5	59.5	60.0	64.0	64.0
Found	58.0	59.4	59.8	60.5	63.5	64.3

Results.—Methyl alcohol (distilled from lime at 64°.5–65°)[2] and commercial benzene (redistilled at 79°–79°.5) were mixed in the proportions by weight, and distilled at the pressures given below. The constant boiling portions analyzed were separated from the excess of either constituent by three fractional distillations in each case.

[1] The difference between the actual specific gravity of a solution of benzene in methyl or ethyl alcohol and that calculated from the specific gravities of the individual liquids was found by Paterno and Montemartini [Gazz. chim. ital., **24**, II, p. 179 (1894), to be so small (1 or 2 in the third decimal place) that it may be disregarded in this method of determination.

[2] The same thermometer was used throughout this and all succeeding investigations. It had been carefully tested, compared with two standard thermometers, and corrected. Whenever the pressure under which a liquid was distilled is not stated, it was approximately 760 mm.

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling-point of fraction analyzed.	Per cent of alcohol found.	Per cent of benzene found.	Ratio of products of vapor-tension and vapor-density.[1]
I	38 : 62	770	58°	38.4	61.6	At 60°, 37.8 : 62.2
II	38 : 62	760	57°.5–58°	39.0	61.0	
III	37 : 63	400	40°	36.8	63.2	At 40°, 35.2 : 64.8
IV	36 : 64	392	39°.5	35.7	64.3	
V	41 : 59	223	25°	33.2	66.8	At 25°, 33.2 : 66.8
VI	34 : 66	223	25°	33.1	66.9	

Ethyl Alcohol and Benzene.

Mixtures of ethyl alcohol (distilled from anhydrous copper sulphate at 77°.5–78°) and benzene (79°–79°.5) were investigated, and it was found that a mixture containing about 32 per cent of alcohol was distilled to the last drop at 67°–68°.

The results of the analysis of distillates under various pressures, obtained as in the case of methyl alcohol and benzene, are as follows :

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling point of fraction analyzed.	Per cent of alcohol found.	Per cent of benzene found.	$\frac{\text{v. t.} \times \text{v. d. of alcohol}}{\text{v. t.} \times \text{v. d. of benzene}}$
I	33 : 67	769	67°–68°	31.4	68.6	At 67°.5, 36.3 : 63.7
II	33 : 67	763	67°–68°	32.3	67.7	
III	33 : 67	421	50°–51°	28.2	71.8	At 50°, 32.3 : 67.7
IV	28 : 72	423	50°–51°	27.6	72.4	
V	28 : 72	241	34°.5–35°.5	23.3	76.7	At 35°, 28.9 : 78.1
VI	23 : 77	243	34°.5–35°.5	23.4	76.6	

To determine the percentage composition of the distillates, 40 cc. were shaken with 50–60 cc. of water.

Twelve analyses of known mixtures gave the following results for the per cent of benzene by volume.

[1] See Berthelot, page 385; and Thorpe, page 386. The values for vapor-tensions throughout these investigations were taken from Landolt and Börnstein's tables, Regnault's values being preferred.

	I.	II.	III.	IV.	V.	VI.
Calculated	60.0	60.0	60.0	65.0	65.0	65.0
Found	59.9	59.9	62.2	65.2	64.8	65.0
	VII.	VIII.	IX.	X.	XI.	XII.
Calculated	65.0	70.0	70.0	70.0	75.0	75.0
Found	66.2	70.1	69.8	70.0	75.0	75.1

General Investigation of the Boiling-points of Binary Mixtures of Liquids Mutually Soluble in all Proportions.

All liquids boiling below 170° that were at hand were purified; and each was mixed with every other whose boiling-point was within 30°–40° of its own, and the mixture distilled. When a constant boiling mixture was found, the ratio of its constituents was determined as nearly as possible by repeated mixing in various proportions, and careful distillation until that ratio was discovered for which the whole mixture distilled most nearly within 1°. A volume of 10–15 cc. was found adequate for each trial mixture distilled.

The ratio of the products of the respective vapor-densities and vapor-tensions at a temperature near that of constant boiling was calculated whenever the necessary data were known, and is given below as the "theoretical ratio."

1. Methyl alcohol (64°.5–65°) and ethyl bromide (37°.5–38°.5) are distilled at 35°–36° (765 mm.) in the approximate ratio of 5 : 95 parts by weight. Theoretical ratio at 35°, 9 : 91 parts by weight.

2. Methyl alcohol and chloroform (60°–61°) at 53°.5–54°.5 (765 mm.); ratio 12 : 88. Theoretical ratio at 55°, 17 : 83.

3. Methyl alcohol and methyl acetate (55°.5–56°.5) at 53°.5–54°.5 (760 mm.); ratio, 18 : 82.

4. Methyl alcohol and ethyl iodide[1] (72°.3–72°.5) at 54°.5–55°.5 (770 mm.); ratio 17 : 83. Theoretical ratio at 55°, 19 : 81.

5. Methyl alcohol and ethyl acetate (75°.5–76°.5) at 61°.7–62°.5 (757 mm.); ratio 47 : 53.

6. Methyl alcohol and benzene. (See p. 388.)

7. Methyl alcohol and isobutyl iodide (118°–119°) at 63°.5–64°.5 (760 mm.). The ratio of 70 : 30 parts by weight gave

[1] See Wanklyn, page 385.

an excess of alcohol. In this and all succeeding distillations of isobutyl iodide mixtures, the formation of tar made a close determination of the proportions impossible.

Methyl alcohol is separated by fractional distillation from ether (34°.5–35°.5), acetone (56°–57°), and toluene (108°.5–109°.3).

8. Ethyl alcohol (77°.5–78°) and ethyl bromide (37°.5–38°.5) at 36°.5–37°.5 (762 mm.). The theoretical ratio at 37°.5 is 6.6 : 93.4. The actual per cent of alcohol seemed to be about half of the theoretical, but could not be more closely determined.

9. Ethyl alcohol and carbon disulphide[1] (45°.5–46°) at 41°.5–42°.5 (755 mm.); ratio, 9 : 91, verified. Theoretical ratio at 43°–44°, 11.4 : 88.6.

10. Ethyl alcohol and chloroform (60°–61°) at 58°.5–59°.5 (759 mm.); ratio, 6 : 94. Theoretical ratio at 60°, 15.6 : 84.4.

11. Ethyl alcohol and ethyl iodide (71°5–72°.5) at 62°.5–63°.5 (761 mm.); ratio, 14 : 86. Theoretical ratio at 60°, 17.4 : 82.6.

12. Ethyl alcohol and ethyl acetate (75°.5–76°.5) at 71°–72° (765 mm.); ratio, 31 : 69.

13. Ethyl alcohol and benzene. (See p. 389.)

14. Ethyl alcohol and isobutyl iodide (118°–119°) at 76°.5–77°.5 (760 mm.); approximate ratio, 70 : 30.

Ethyl alcohol is separated from propyl alcohol (97°.5) and toluene (108°.7–109°.3).

15. Isopropyl alcohol (81°–82°) and carbon disulphide (45°.5–46°) at 43°.5–44°.5 (761 mm.); ratio, 9 : 91.

16. Isopropyl alcohol and ethyl iodide (71°.5–72°.5) at 65°.5–66°.5 (764 mm.); ratio, 13 : 87.

17. Isopropyl alcohol and ethyl acetate (75°.5–76°.5) at 74°–75° (770 mm.); approximate ratio, 26 : 74.

18. Isopropyl alcohol and benzene (79°–79°.5) at 71°–72° (758 mm.); ratio, 30 : 70.

19. Isopropyl alcohol and water at 78°.5–79°.5 (768 mm.); ratio, 89 : 11.[2]

[1] See Berthelot, page 385.

[2] See Linnemann, page 386. The per cent of water in the compounds $3C_3H_8O.2H_2O$, $2C_3H_8O.H_2O$ and $3C_3H_8O.H_2O$ is 16.7, 13, and 9 per cent, respectively. The alcohol used by me was distilled from lime at 81°–82°. This case should be investigated further.

20. Isopropyl alcohol and isobutyl iodide (118°–119°) at 81°–82° (761 mm.); approximate ratio, 70 : 30.

Isopropyl alcohol is separated from chloroform (60°–61°) and toluene (108°.7–109°.3).

21. Normal propyl alcohol (95°.7) and ethyl iodide (72°.3–72°.5) at 69°.5–70°.5 (768 mm.); approximate ratio, 7 : 93.

22. Propyl alcohol and benzene (79°–79°.5) at 76°–77° (762 mm.); ratio, 16.5 : 83.5. Theoretical ratio at 80°, 28.5 : 71.5.

23. Propyl alcohol and water at 87°–87°.5 (770 mm.); ratio, 72 : 28.[1] Theoretical ratio at 87°.5, 79 : 21.

24. Propyl alcohol and toluene (108°.7–109°.3) at 91°–92° (765 mm.); ratio, 53 : 47.

25. Propyl alcohol and isobutyl iodide (118°–119°) at 92.5°–93°.5 (753 mm.); approximate ratio, 45 : 55.

Normal propyl alcohol is separated from ethyl acetate (75°.5–76°.5) and isobutyl alcohol (105°.3–106°.3).

26. Isobutyl alcohol (105°.3–106°.3) and toluene (108.8°–109°.3) at 100° (764 mm.); ratio, 43 : 57.

27. Isobutyl alcohol and isobutyl iodide (118°–119°) at 101°–102° (765 mm.). The ratio of 33 : 67 gave an excess of alcohol.

28. Isobutyl alcohol and ethylene bromide (129°–130°) at 104°.5–105°.5 (763 mm.); approximate ratio, 62 : 38.

Isobutyl alcohol is separated from ethyl iodide (72°.3–72°.5), benzene (78°.5–79°), and metaxylene (136°–137°).

29. Amyl alcohol (128°–129°)[2] and isobutyl iodide (118°–119°) at 115°–116° (765 mm.). The ratio of 20 : 80 gave a slight excess of iodide.

30. Amyl alcohol and ethylene bromide (129°–130°) at 121°–122° (760 mm.); ratio, 30 : 70. Ratio of vapor-densities, 32 : 68.

31. Amyl alcohol and metaxylene (136°–137°) at 125°–126° (760 mm.); ratio, 52 : 48. Amyl alcohol and paraxylene (137°–137°.5) at 125°–126°, in the same ratio; and amyl alcohol and orthoxylene (140°–141°) at 127°–128°, with a slightly larger per cent of alcohol.

[1] See Konowalow, page 386; and Ramsay and Young, page 387. My determination of the ratio was made before I knew of that found by Ramsay and Young.

[2] This was obtained by repeated fractionation from the commercial mixture of amyl alcohols.

Amyl alcohol is separated from toluene (108°.8–109°.3).

32. Allyl alcohol (95°–96°) and benzene (79°–79°.5) at 76°–77° (760 mm.). The ratio of 20 : 80 gave a slight excess of alcohol.

33. Allyl alcohol and toluene (108°.8–109°.3) at 91°–92° (756 mm.); approximate ratio, 50 : 50.

34. Acetic acid (117°–118°) and toluene (108°.8–109°.3) at 103°.5–104°.5 (761 mm.); ratio, 30 : 70.

35. Acetic acid and metaxylene (136°–137°) at 113°.5–114°.5 (761 mm.); ratio, 27 : 73.

Acetic acid is separated from carbon disulphide (45°.5–45°.7) and benzene (79°–79°.5).

36. Butyric acid (159°–160°) and water at 99°–99°.5 (763 mm.); ratio, 20 : 80.[1] Theoretical ratio at 100°, 32 : 68.

37. Butyric acid and brombenzene (152°–153°) at 147°–148° (748 mm.); ratio, 19 : 81.

38. Ether (34°.5–35°.5) and carbon disulphide (45°.5–46°) at 34°.5–35°.5 (768 mm.); approximate ratio, 65 : 35. Theoretical ratio at 35°, 59 : 41.

Ether is separated from acetone (56°–57°) and chloroform (60°–61°). A mixture of ether and ethyl bromide (37°.5–38°.5) is distilled at the same temperature (35°–38°) as its constituents.

39. Carbon disulphide (45°.5–45°.7) and ethyl bromide (37°.5–38°.5) at 37°–38° (770 mm.); ratio 32 : 68. Theoretical ratio at 37°.5, 35 : 65.

40. Carbon disulphide and acetone (55°.5–56°.5) at 38°.5–39°.5 (766 mm.); ratio, 74 : 26. Theoretical ratio at 40°, 66 : 34.

41. Carbon disulphide and methyl acetate (55°.5–56°.5) at 39°–40° (756 mm.); ratio, 71 : 29.

42. Carbon disulphide and ethyl acetate (75°.5–76°.5) at 45°.5–46°.5 (768 mm.); ratio, 92 : 8.

Carbon disulphide is separated from chloroform (60°–61°), ethyl iodide (71°.5–72°.5), and benzene (79°–79°.5).

43. Acetone (55°.5–56°.5) and methyl acetate (55°.5–56°.5) in about equal parts are distilled 0°.5 below the boiling-point of either.

[1] See Konowalow, page 386.

44. Acetone and ethyl iodide (71°.5–72°.5) at 55°–56° (770 mm.); approximate ratio, 60 : 40.

45. Acetone and chloroform (60°–61°) at 64°–65° (760 mm.); approximate ratio, 20 : 80.

Acetone is separated from ethyl bromide (37°.5–38°.5) and ethyl acetate (75°.5–76°.5).

46. Chloroform (60°–61°) and methyl acetate (55°.5–56°.5) at 64°–65° (760 mm.); approximate ratio, 78 : 22.

Chloroform is separated from ethyl bromide (37°.5–38°.5), ethyl iodide (71°.5–72°.5), ethyl acetate (76°–77°), and benzene (79°–79°.5).

47. Ethyl iodide (71°.5–72°.5) and ethyl acetate (75°.5–76°.5) at 69°.5–70°.5 (762 mm.); approximate ratio, 78 : 22.

48. Ethyl iodide and benzene (79°–79°.5) at 74°–75° (758 mm.); approximate ratio, 80 : 20.

Ethyl acetate (75°.5–76°.5) is separated from benzene (79°–79°.5).

Isobutyl iodide (118°–119°) is separated from toluene (108°.7–109°.3).

Acetone (55°.5–56°.5) and benzene (79°–79°.5) in the ratio of 5 : 1 approximately, showed a tendency to gather at 57°–58°, this fraction constantly increasing throughout the course of repeated distillations. But the proportions could not be found for which all of the mixture would boil at this point, as in every case there were small fractions from 57° to 79°.

Ethylene bromide (129°–130°) and metaxylene (136°–137°), in the ratio of 5 : 2 approximately showed a similar tendency to gather at 130°–131°.

Amyl alcohol (128°–129°) and brombenzene (152°–153°), in the ratio of 5 : 2 approximately seemed to be distilled at 128°–129°, but the small per cent of the latter and the formation of tar prevented a definite determination.

Summary.—Of the 80 mixtures examined, 45 were distilled at a constant temperature at or below the boiling-point of the more volatile constituent; 2[1], at a constant temperature above the boiling-point of the less volatile constituent; 1,[2] at a constant temperature between the boiling-points of the constitu-

[1] Nos. 45 and 46. [2] No. 48.

ents; 1,[1] in which the boiling-points of the constituents are too close for fractionation, presents no relative depression or elevation of the boiling-point of the mixture; and 3 are of an uncertain character.

Boiling-points of Mixtures of Liquids whose Mutual Solubilities are Limited.

Two cases of this kind were examined.

1. Isobutyl alcohol (105°.3–106°.3) saturated with water at the temperature of the room (about 5 parts of alcohol to 1 part of water) boils for a time at the constant temperature of 89°–90°, the distillate separating in the receiver into two layers. The excess of alcohol above the amount necessary for the proportions of distillation at constant temperature causes the temperature to rise gradually to 106°. If the alcohol is saturated at higher temperatures, the portion distilling at 89°–90° is correspondingly larger.

2. Methyl alcohol (64°.5–65°) saturated with carbon disulphide (45°.5–46°) (about equal parts by weight at the temperature of the room) boils for a time at 37°–38°. The excess of alcohol causes the temperature to rise ultimately to 65°. This mixture shows phenomena similar to those noted in case 1.

Conclusions.

1. The large proportion of constant boiling mixtures found in the cases examined makes it evident that this phenomenon is by no means so exceptional as has hitherto been supposed. In fractional distillation one should always be on his guard against it.

2. The changes in the composition of the distillates, corresponding to the changes in pressure and temperature of the distillation, indicate that the two mixtures investigated[2] are not true chemical compounds, and that any approximation to molecular proportions must be regarded as accidental.

3. It is well known that two liquids mutually insoluble are distilled at a constant temperature in the ratio of the products of their respective vapor-densities and vapor-tensions at the temperature of distillation.

[1] Ether-ethyl bromide.

[2] See pages 388 and 389.

If the liquids are partially soluble in each other, they are also distilled at a constant temperature, but with some deviation from this ratio, so long as there are two layers of liquids in the distilling flask.

The results of this investigation are generally in accord with the theory that when two liquids, mutually soluble in all proportions, are distilled at a constant temperature, their ratio in the distillate is that of the products of the vapor-densities and vapor-tensions of the pure liquids at that temperature, modified more or less by their influence upon each other.[1]

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF BENZOYL CHLORIDE ON THE PHENYLHYDRAZONES OF BENZOIN.[2]

By Paul C. Freer.

In a previous paper,[3] while discussing the constitution of the phenylhydrazones of benzoin, I described a body, melting at 163°, produced by the action of benzoyl chloride on β-benzoin phenylhydrazone. This substance, owing to analyses and molecular weight determinations in methyl oxalate solution, I presumed to be a third isomeride of the chemical individuals under consideration. The ease with which the reaction takes place (at 0°) and the fact that the benzoyl chloride only in part disappears pointed to this conclusion, but my inability to account for such a body satisfactorily, as well as its appearance, caused me to reinvestigate the entire reaction thoroughly and with large quantities of material. The result was most surprising, for it showed that even at 0° benzoyl chloride accomplishes what I have never before observed with phenylhydrazones; namely, the severance of the two nitrogen atoms in the phenylhydrazine molecule, with the production of benzanilide, which latter substance is the supposed γ-benzoin phenylhydrazone. The two bodies have nearly identical carbon and hydrogen, the difference being in the nitrogen

[1] The greatest deviation from the calculated ratio was found in the mixture of propyl alcohol and benzene (No. 22).

[2] This article, which was sent from Germany by the author, reached the editor while the article by Professor Alexander Smith (**22**, 198), calling attention to the same errors, was in press.

[3] This Journal, **21**, 45.

and molecular weight determinations, which the subsequent examination proved to have been in error. The accurate results are very interesting and are consequently given in detail.

Sixty-five grams of pure β-benzoin phenylhydrazone were dissolved in 350 cc. of dry ether and, after 32.5 grams of pure benzoyl chloride, free from hydrochloric acid, had been added the whole was placed in an atmosphere of carbon dioxide and kept at winter temperature for two days. A slightly pink precipitate weighing 27.5 grams separated out. This was filtered, dried in a current of carbon dioxide, and then thoroughly washed with water until there was no further change; the precipitate then weighed 21 grams, and the water, when neutralized and mixed with the exact amount of silver nitrate, precipitated 8 grams of silver chloride, corresponding to 2.03 grams of hydrochloric acid. The filtrate from the silver chloride was preserved. The original organic precipitate was recrystallized from alcohol and yielded 11 grams of pure benzanilide, identified by its melting-point, molecular weight, combustions, and by its form of crystallization examined, with a sample prepared in another way, according to Lehmann's method with the microscope. The mother-liquors from this recrystallization were then carefully precipitated with water until all of a tarry substance had separated (weight 2.5 grams), and the remainder, after further dilution, was repeatedly extracted with ether, the ether dried and evaporated. There remained a crystalline mass, permeated with some oil, having the odor of benzaldehyde. The crystals were dried on a porous plate and recrystallized from boiling alcohol, in which they were sparingly soluble. These white, feathery needles, melting at 273°–275°, contained 9.6 per cent nitrogen, the calculated amount for $C_{21}H_{17}N_3$ being 9.4 per cent. A comparison of this body with lophine, prepared by the usual method, proved its complete identity. The mother-liquors, after all lophine had been extracted, were evaporated to dryness, leaving 1 gram of a crystalline remainder, which proved to be a mixture of ammonium and aniline salts.

The ethereal filtrate from the original precipitate was evaporated *in vacuo* until nothing but a reddish tar, weighing 67

grams, was left. This was extracted four times with a boiling mixture of one-third ligroin and two-thirds ether. The yellow solution contained all of the unchanged benzoyl chloride and, on evaporation, yielded a mass of needles. These were spread on a porous plate, to remove the liquid impurity, and when dried weighed 19 grams. Recrystallized from alcohol they melted at 96° and were pure benzil, while 3.5 grams of dibenzanilide were obtained from the mother-liquors. The tar, remaining after the above extraction, was then boiled out twice, each time during two hours, with concentrated hydrochloric acid, and then filtered. On standing, the filtrate separated 2.5 grams of benzoic acid and on evaporating it left 7 grams of a crystalline residue. This was extracted with absolute alcohol (the solution turning deep-blue owing to the presence of small quantities of a dye) and the insoluble remainder, tested by the Kjeldahl method, proved to be pure ammonium chloride. The alcohol also extracted a small quantity of the salt of an organic base. There remained unaltered 31.5 grams of a black tar, which was heated to 190° in a sealed tube for several hours with concentrated hydrochloric acid. As a result some more benzoic acid and ammonium chloride was obtained, but 25 grams remained unaltered even at 200°.

The products of the action of benzoyl chloride on β-benzoin phenylhydrazone, in absolute ethereal solution, at winter temperature, are therefore as follows :

The total quantity of phenylhydrazone taken was 65 grams; that of benzoyl chloride was 32.5 grams.

Found.	Grams.
Pure benzanilide	11
Lophine	5
Benzil	11
Dibenzanilide	3.5
Hydrochloric acid	2.03
Ammonium chloride } Aniline hydrochloride }	1.00
Unchanged benzoyl chloride	8.30
Tar	50.5
Total	94.33

In all other cases in which any crystalline bodies at all have been obtained by the action of benzoyl chloride on phenylhydrazones, these substances have been either mono- or dibenzoylphenylhydrazine or benzoylated phenylhydrazones, but in the case of β-benzoin phenylhydrazone not a trace of these latter products could be discovered. As a consequence, the inference must be drawn that either the body under discussion is not a phenylhydrazone at all or that, by the action of benzoyl chloride, it is first converted into a different substance. The first supposition is scarcely admissible, so that only the second one remains. In order to test this view the action of benzoyl chloride on β-benzoin phenylhydrazone methyl ether was tested. In this case, although a reaction slowly sets in, none of the above products could be obtained, with the exception of some ammonium chloride and traces of benzaldehyde, the remainder being a non-crystallizable tar, and the conclusion that the hydroxyl group is necessary for the above reaction is therefore justified.[1] The first action of benzoyl chloride would therefore be one of dehydration with the production of a body of the structure,

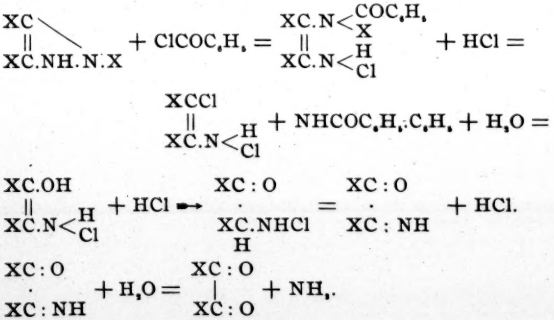
$$\begin{matrix} C_6H_5C \diagdown \\ \quad\quad\quad\quad \| \\ C_6H_5C.NH.N.C_6H_5, \end{matrix}$$

and such a substance could then be decomposed with the separation of an aniline instead of a phenylhydrazine derivative. The nature of the decomposition, whether the benzanilide is the result of hydration and decomposition of the first product of the reaction, or whether it is formed by the addition of benzoyl chloride, as well as the origin of the benzil and lophine, is still undecided, so that the next step in the study of the reaction would be an examination of the action of a substituted benzoyl chloride on β-benzoin phenylhydrazone.

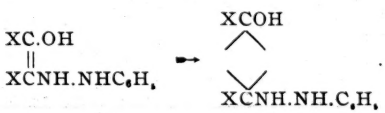
Ten grams of β-benzoin phenylhydrazone and 9 grams of pure *m*-nitrobenzoyl chloride were dissolved in 100 cc. of absolute ether and allowed to stand at winter temperature. After two hours a small quantity of a black tar, apparently

[1] Experiments with desoxybenzoinphenylhydrazone demonstrates that it behaves very differently from the corresponding benzoin derivative. It is an easily oxidized phenylhydrazone, yielding explosive derivatives, and must therefore be classified with the phenylhydrazones of acetone and acetophenone, as a hydrazo obdy.

an oxidation-product, had separated, and the solution had turned dark-red. This tar was separated, washed with alkali, extracted with ether, and dried; the remainder was non-crystallizable, and only a small quantity of benzil could be obtained from it by extraction with ligroin. The original ethereal solution was once more placed in the cold. After twenty-four hours hard, warty crystals which, when recrystallized from alcohol, melted at 153°, and, on comparison with a product obtained in a different manner, proved to be *m*-nitrobenzanilide were obtained. After the last traces of this body had been formed, the original solution was evaporated in a vacuum, leaving a black tar which had the odor of nitrobenzoyl chloride and, as a result of the presence of this body, was deliquescent. This tar was repeatedly extracted with warm ligroin and the solvent distilled, leaving a crystalline mass. This was covered with a solution of sodium carbonate, to remove unchanged *m*-nitrobenzoyl chloride, and the remainder was then recrystallized from alcohol, and proved to be pure benzil. No lophine, or at least a quantity too small to be identified, could be isolated. The benzanilide and benzil are therefore directly produced by the action of benzoyl chloride on β-benzoin phenylhydrazone. The reaction must therefore be one of addition, separation of hydrochloric acid and hydration, the dibenzanilide, of course, being produced by the action of benzoyl chloride on benzanilide. Benzilimide would also result as an intermediary product.



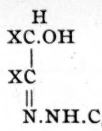
This series of reactions seems the only way in which to account for the simultaneous production of benzanilide, benzil, and ammonia in about equivalent quantities, the water necessary for the reaction being furnished by the first dehydration. The lophine and tar now remain unaccounted for. The former cannot be produced by a reaction which involves the addition of benzoyl chloride to form a new molecule, otherwise nitrolophine would have appeared among the products of the action of *m*-nitrobenzoyl chloride on β-benzoin phenylhydrazone. The lophine must therefore result directly from the hydrazone, and it can only do so by means of the intervention of benzaldehyde, and the odor of the latter, which is markedly present among the first reaction-products, is proof of its formation. The benzaldehyde is not formed by hydration of β-benzoin phenylhydrazone, for then an equimolecular quantity of benzal phenylhydrazone would result, and none of the latter body could be detected. There seems only one conclusion possible, therefore, and that is the dissociation of the β-benzoin phenylhydrazone with the formation of divalent carbon atoms:



The benzaldehyde with benzil and ammonia in the nascent state would form lophine, while the remainder of the molecule of the hydrazone, in conjunction with benzoyl chloride, would condense to form the tar rather than, by a rearrangement, benzal phenylhydrazone. This accounts for the fact that the tar, on heating with hydrochloric acid, yields benzoic acid, ammonia, aniline, and certain amounts of a blue dye. The only means of explanation for this complex reaction is therefore in the assumption that addition and dissociation reactions take place simultaneously.

As was mentioned in my previous paper, and as I have again convinced myself in this case, α-benzoin phenylhydrazone does not react with benzoyl chloride under the above circumstances; *i. e.*, at winter temperature. If the difference

between the two bodies is one of geometric isomerism, and if they are both true phenylhydrazones this fact could be easily explained by the assumption that the β-hydrazone is the *cis* modification in regard to the hydroxyl group,



while the α is the *trans*. The formation of benzil, benzanilide, and lophine cannot, however, be explained with this formula as a basis, without assuming extensive intramolecular changes. I was surprised, however, to discover that *m*-nitrobenzoyl chloride reacts with α- in exactly the same way as it does with β-benzoin phenylhydrazone. With either theory as a basis, this behavior can only be explained by the assumption that the more reactive nitro chloride is able to transform the α-into the β-body, but as the latter would inevitably be destroyed by the nitrobenzoyl chloride which is present, no absolute proof of this can, of course, be furnished.

The best proof of the hydrazo structure of β-benzoin phenylhydrazone at present rests upon the fact that it yields the red nitrogen trioxide addition-product and the perbromide of the latter, described in my previous paper, but unless the azo derivative, similar to the ones obtained by me from other hydrazones, can be isolated, a definite decision in either direction cannot be reached.

MUNICH, August, 1899.

Contribution from the Kent Chemical Laboratory of Yale University.

NOTES ON THE SPACE ISOMERISM OF THE TOLUQUINONEOXIME ETHERS.

BY WM. CONGER MORGAN.

In an article on the "Ethers of Toluquinoneoxime and their Bearing on the Space Isomerism of Nitrogen."[1] published from this laboratory, it was stated that the methyl, acetyl, and benzoyl ethers of toluquinonemetaoxime, whether

[1] Bridge and Morgan: This JOURNAL, **20**, 761.

formed by the action of hydroxylamine on the quinone or by nitrous acid on the corresponding cresol, showed evidence of existing in isomeric forms. Of these bodies the benzoyl ether received the most careful investigation, and by fractional crystallization, from the crude reaction-product, two portions were obtained, one readily separating from an alcoholic solution in the form of yellow crystals melting at 193°, while a second body, melting approximately at 144°, was never obtained in a state of purity. The fact that from this lower-melting fraction, on recrystallization, a portion of the higher-melting body was always obtained, suggested the possibility that the solvent might have a tendency to cause a transition from one isomer to the other. Since, however, after repeated crystallizations from boiling alcohol a low-melting fraction was obtained, and therefore such rearrangement was evidently incomplete, the action of alcohol under pressure on the different fractions was investigated. From a portion of the ether melting at 139°, heated for three hours in a closed tube to 120°, the product melting at 193° crystallized in a characteristic form and no crystals were obtained melting lower than 180°. On treating the higher-melting isomer in the same way, no action was observed until the temperature was raised above 150°, when complete decomposition ensued.

In order to ascertain, if possible, a direct method of transition from one form into the other, the action of alkalies, among other reagents, was tried. No change other than a hydrolytic cleavage was observed, and this was readily completed on warming. By saponifying a fraction melting completely at 142° and treating the isolated oxime in the usual way with benzoyl chloride, the benzoyl ether was again obtained, liquefying at 193°, and, although there was a trifling irregularity in the melting-point of some of the crystals, no low-melting fraction was isolated. On similar treatment of a portion melting at 193° the original ether was obtained, but none of the low-melting isomer.

From these facts it is obvious that the isomer existing in a much smaller proportion in the crude reaction-products, present as the principal constituent in the low-melting fractions, must be regarded as the labile form, tending to go over into

the stable form under the influence of boiling alcohol or during the process of a chemical reaction. This action of alcohol increases the difficulty of isolating the labile form and naturally suggests the idea of using other solvents; but imperfect as was the separation of the two isomers, better results were obtained from an alcoholic solution than by any other means.

The phenomena described in the article to which reference was previously made, have been reproduced completely in the ethers made by the action of acid chlorides on the sodium salt of the oxime (to be described later) produced by the action of pure amyl nitrite on the sodium salt of the cresol. In the resulting metathesis, as in the product of the reaction of hydroxylamine on the quinones, there is not the possibility of the formation of a nitro body as there is in the action of free nitrous acid on the cresols. Consequently the interfering action of an admixture of such a body with the oxime ethers cannot influence the results as obtained, yet the presence of a low-melting body existing in a larger proportion in this product than in the substances formed by the agency of free nitrous acid according to the type fraction, was indisputably evidenced. The identity of the observed phenomena under varying conditions and methods of formation, thus removing the probability of an admixture of an impurity and at the same time of a structural difference, seems to establish the hypothesis of a space isomerism in the case of the ethers of toluquinonemetaoxime.

Inasmuch as the monohalogen derivatives of the quinoneoxime ethers are beautifully crystalline bodies, it was thought advisable to prepare the monochlor- and monobrombenzoyl ethers of toluquinoneorthooxime in the hope of obtaining from these well-characterized products additional evidence as to the existence of isomeric phenomena in the orthooxime ethers. Although there was the possibility of both "space" and "place" isomerism neither body offered any indication of the presence of isomers of any kind, but each appeared to be an entirely homogeneous and simple substance, liquefying sharply at a definite melting-point.

EXPERIMENTAL PART.

The Sodium Salt of Toluquinonemetaoxime.

The sodium salt was prepared according to the general method suggested by Walker.[1] To a molecule of sodium alcoholate freshly prepared by dissolving metallic sodium in as little alcohol as possible, a molecule of the orthocresol was added and the solution treated with slightly more than the theoretical quantity of amyl nitrite, the whole being thoroughly mixed together. On standing in a vacuum over sulphuric acid, the sodium salt separates in fine purple crystals, which, on washing carefully with ether to remove amyl alcohol and excess of nitrite, is ready for use. It may be recrystallized from dilute alcohol if further purification is desired. This salt is extremely soluble in water, much less in alcohol, and insoluble in most other organic liquids. On standing in the air it tends to decompose, turning almost black. On analysis:

0.1231 gram, dried over H_2SO_4, gave 0.0541 gram Na_2SO_4.

	Calculated for $C_7H_4O_2NNa$.	Found.
Na	14.48	14.26

Monobromtoluquinone-o-oxime Benzoyl Ether.

This ether was obtained from the dibromide previously described[2] by boiling with dilute 75 per cent alcohol, during which process hydrobromic acid is split off. Being much less soluble in alcohol than the dibromide, the monobrom body separates from the solution as soon as formed and may be obtained as a yellow crystalline powder by filtration of the cooled liquid. On analysis,

0.1450 gram, dried over H_2SO_4, gave 0.2774 gram CO_2, and 0.0415 gram H_2O.

0.1102 gram gave 0.0643 gram AgBr.

	Calculated for $C_{14}H_{10}Br.NO_2$.	Found.
C	52.49	52.17
H	3.15	3.18
Br	24.98	24.83

On crystallizing from alcohol the ether was readily obtained

[1] Walker: Ber. d. chem. Ges., **17**, 399.

[2] Bridge and Morgan: This JOURNAL, **20**, 776.

in two, apparently unlike, modifications, one being long prismatic crystals, the other appearing as broad, thick, monoclinic plates. It was at first believed that this distinction in crystal form was due to the presence of isomeric bodies, but no difference in melting-point could be found since each portion liquefied sharply at 184°. Under the lens, moreover, the plates are seen to be striated parallel to one edge and have all the appearance of consisting of a number of the simple crystals united to each other, since both forms are plainly of the same system. Slow cooling was found to be productive of the massed crystals.

Toluquinone-o-oxime Benzoyl Ether Dichloride.

The benzoyl ether was dissolved in a small amount of chloroform and dry chlorine gas passed into the solution. The action is very rapid and after fifteen minutes the liquid may be allowed to evaporate and the white product, crystallized once from glacial acetic acid, melts sharply to a colorless liquid at 149° without decomposition. Fractional crystallization does not change the melting-point except as the action of the solvent causes a slight formation of the monochlor body. On analysis,

0.1241 gram, dried over H_2SO_4, gave 0.2431 gram CO_2, and 0.0424 gram H_2O.

0.2105 gram gave 0.1930 gram AgCl.

	Calculated for $C_{14}H_{11}Cl_2NO_2$.	Found.
C	53.84	53.42
H	3.55	3.80
Cl	22.72	22.67

The dichloride, like the dibromide, is slightly soluble in alcohol, readily soluble in chloroform, glacial acetic acid, and fuming nitric acid. Water precipitates the ether entirely unchanged from the two last-mentioned solvents. In crystal form it resembles very closely the dibromide, separating from a boiling acetic acid solution in short, thick, colorless, almost microscopic prisms, suggesting the orthorhombic system. In point of stability this ether, as well as the monochlor body, far surpasses the corresponding bromine compounds.

Monochlortoluquinone-o-oxime Benzoyl Ether.

Analogous to the dibromide, by the action of dilute alcohol on the dichloride, hydrochloric acid is split off and a yellow monochlor substitution-product is formed, one hour being sufficient to complete the reaction. This ether closely resembles the monobrom derivative in properties and in crystal form. The product as obtained from an alcoholic solution will decompose and melt at a temperature varying ordinarily from 185°–193°, depending on the rapidity with which the heat is applied. "Dipped" for fifteen seconds, the crystals melt without decomposition at 200°. Although carefully fractioned from alcohol, ligroin, and benzol, the substance appeared to be entirely homogeneous, and no variation in the melting-point was observed. On analysis,

0.1209 gram, dried over H_2SO_4, gave 0.2688 gram CO_2, and 0.0424 gram H_2O.

0.1035 gram gave 0.0533 gram AgCl.

	Calculated for $C_{14}H_{10}Cl.NO_2$.	Found.
C	60.97	60.63
H	3.66	3.90
Cl	12.87	12.75

JUNE, 1899.

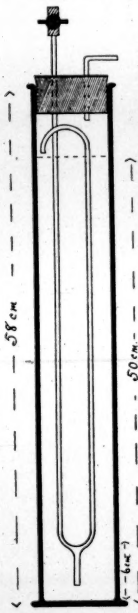
A DISSOLVER.

BY ARTHUR JOHN HOPKINS.

An apparatus for hastening the solution of salts has been described by Richards.[1] That such devices will supplant the good old methods of heating or stirring is not to be supposed; but heating is often proscribed by the nature of the salt or the requirement of a constant temperature, and stirring by hand is laborious and inconstant; and although both constant temperature and constant circulation are supplied by mechanical stirrers, yet it is possible that the necessity for mechanical devices has deterred many a chemist from entering upon the study of solubilities. A field may therefore be open for an apparatus serving the same purpose as a stirrer and constructed from material with which the chemist is already familiar.

[1] This JOURNAL, **20**, 189.

Richards' dissolver, although of simple construction, is very efficient and moreover is automatic, in that it requires no stirrer. Its efficiency is obviously limited to such salts as can form saturated solutions of much greater specific gravity than the solvent and further limited to the formation of non-saturated solutions of these salts. The rate of flow in a purely automatic dissolver will rapidly approach zero, as the specific gravity of the solvent gains on that of the saturated solution. In fact, at any one moment the rapidity of solution varies as the square of the velocity of the solvent passing the crystals.



In the hope of making a dissolver which shall be universally applicable without resorting to mechanical stirrers, an attempt has been made in this laboratory to apply a well-known device to this problem. The result is a dissolver of simple construction and great efficiency, which will rapidly prepare solutions of any specific gravity.

The accompanying illustration shows such an apparatus. An ordinary glass cylinder of any convenient size may be used. The one represented holds 2200 cc.[1] Through one hole of a two-holed stopper is passed a straight glass tube of about 6 mm. bore, fitted at the upper end with a short rubber tube and screw-cock. The lower end of this glass tube is fused, or bound by aid of rubber connection tubing, to one arm of a Y-tube, the lower arm of which reaches nearly to the bottom of the cylinder. The third arm of the Y-tube meets a second glass tube, which reaches up nearly to the stopper and there curves down to give direction to the concentrating solution. The second hole of the stopper carries a short exit tube bent at a right angle, the lower portion of which extends to a point just below the bottom of the stopper.

To use the dissolver, introduce the desired quantity of

[1] It is best to choose a cylinder of such size that the quantity of solution desired shall fill it to a point just below the curved tube.

water or other solvent with the weighed quantity of salt to be dissolved, then put the stopper, carrying its tubes, firmly into position, and apply, by means of a filter-pump attached to the short right-angled tube, enough suction to overcome the water pressure of 44 cm. A current of air, regulated by the screw-cock to prevent vibrations in the Y-tube, follows the water down the long tube in continuous column, but continues only as far as the junction of the Y-tube, for there it is broken into little columns alternating with columns of the saturating solution drawn up through the lower arm of the Y-tube. These broken columns of air, rising through the curved tube, lift the solution drawn directly from the crystals, and throw it out upon the least saturated solvent at the top. The air escapes through the short tube, and the fresh solvent, which occupied the upper position in the cylinder at the beginning, sinks down to dissolve more of the crystals below. When a carefully regulated and not too great suction is applied, there is a continuous and rapid current of the solution passing the crystals while the saturated solution may be seen streaming from the crystals to the lower end of the Y-tube.

To test the efficiency of this apparatus, 30 grams of copper sulphate in crystals of about 2 grams each were dissolved in 200 cc. of distilled water at 19°. For this purpose a cylinder of about one-tenth the size described was selected. Complete solution took place in about forty minutes.

In order to prepare a solution of ammonium carbonate for use in qualitative analysis, a very large stand-cylinder which had formerly served as a generator of hydrogen sulphide, was employed. The proper tubes were attached to the stopper and when 1 kilo of commercial ammonium carbonate, 1 liter of concentrated ammonium hydroxide, and 4 liters of distilled water had been placed in the stand-glass, suction was applied, and in thirty minutes all but about 20 grams of the salt had been dissolved. Dissolving this salt in such large quantities by the usual method takes not less than four or five consecutive hours, and in busy laboratories a day or two of intermittent stirring is often allowed. Assembling the parts of the apparatus and affecting the solution, in the case cited, required less than forty-five minutes.

This dissolver has been used, in a bath of constant temperature, for making saturated solutions of copper sulphate and for determining the solubility of this salt at different temperatures. For this purpose the lower end of the short reduction tube was protected and the entering air was washed through caustic potash and then through sulphuric acid, and again washed on leaving through weighed sulphuric acid tubes. Completely saturated solutions were obtained in about ninety minutes. This work will be taken up again in this laboratory and reported upon.

The dissolver here described, like that of Richards, requires no attention and is very easily constructed in a few minutes from ordinary laboratory material. It involves no mechanical difficulties, is universally applicable, and seems as rapid as any of the mechanical stirrers or shakers.

AMHERST COLLEGE, 1899.

OBITUARY NOTICES.

EDWARD FRANKLAND.

The deaths of Bunsen and Frankland, both of which have occurred during the summer, have left a sad vacancy in the ranks of those who were so active about the middle of the century, during a critical period of the development of the science of chemistry, the formative period of its theories. Frankland, who was born Jan. 18, 1825, died August 9th, in Norway, where he was accustomed to spend his summers. Although in his seventy-fifth year his vigor and activity made him appear much younger. After being educated at the Grammar school of his native town and acting as one of the science masters at Queenwood College, he went to Germany and came under the influence of Liebig and Bunsen. In 1851 he returned to England and was appointed professor at Owens College, Manchester, which place he left in 1857 to take charge of the chemical department of St. Bartholomew's Hospital Medical School in London. In 1863 he was appointed Fullerian professor of chemistry in the Royal Institute and in 1865 succeeded Hofmann in the chair which was afterwards transferred to the Royal School of Mines at South Kensington. He occupied this position until he retired in 1885. He was honored by election to membership in many societies at home and abroad, was president of the Chemical

Society in 1871–72, foreign secretary of the Royal Society for the past five years, and received the Copley medal in 1894. He was knighted in 1897 for his activity as water analyst for more than twenty years. Following the example of Liebig and others, who were at that time vigorous supporters of the radical theory, Frankland attempted to isolate the much sought for radicals. He obtained a product which he considered to be the radical C_2H_5, but which was shown later to be C_4H_{10}. Shortly afterwards, in a paper entitled "On a New Series of Organic Compounds containing Metals" he describes the organo-metallic compounds. According to the views of Kolbe, which were widely accepted at that time, all organic compounds could be explained as copulated radicals, an explanation, however, that was not satisfactory even to Kolbe. Frankland soon recognized that the organo-metallic compounds could not be explained in this way, but that each element had a saturating capacity as regards other elements. He found that these ideas of the definite saturating capacity of elements could be applied to both inorganic and organic compounds, and Kolbe recognized the value of these ideas and modified his ideas of copulae to conform to the views as expressed by Frankland, who said that "no matter what the character of the uniting atoms may be, the combining power of the attracting element is always satisfied by the same number of these atoms." He recognized that the atoms of the metals and metalloids, in their power of uniting with the radical of alcohol, with halogens and oxygen possessed a varying but, within certain limits, definite saturating capacity. These ideas, in which we find the first clear view of our present theory of valence, were very slowly accepted, and it was not until the appearance of Kekulé's papers "On the Constitution of Chemical Compounds" that their value was recognized. The quadrivalence of carbon, which is so often claimed to have originated with Kekulé, had already been recognized by Kolbe and Frankland, and it was the suggestion as to "the linkage of atoms" for which we are especially indebted to Kekulé. Since his appointment, in 1863, as a member of a Royal Commission on the Pollution of Rivers and Domestic Water Supply, Frankland has been greatly interested in this subject and has been one of the greatest authorities on the analysis of drinking-water. J. E. G.

Robert Wilhelm Bunsen.

The chemists of the whole world, and especially the elder ones who were so fortunate as to come in personal relationship with Bunsen, will regard his death, which occurred August

16th, as a personal grief, for not only was he respected and looked up to as a great investigator, but he was loved as a teacher and a friend. His wonderful skill in experimenting and his genius which was so strongly manifested in his patient teaching endeared him to many who came under his influence. His simple and unpretentious manner made him a great favorite in the university life at Heidelberg. He spent his life in a university atmosphere as his father was a distinguished Göttingen professor. Born in 1811, he graduated as a Ph.D. at Göttingen in 1831. The next five years he spent in studying in Paris, Berlin, and Vienna, and in 1836 succeeded Wöhler at Cassel. From there he was called to Marburg, then to Breslau, where he only remained a short while before he was called to become professor at Heidelberg, to remain one of that university's distinguished faculty until his resignation in 1889. The first work to which our thoughts turn, when his name is mentioned, is that on the organic compounds of arsenic, now regarded as one of the classics of chemistry. His work, in conjunction with Kirchhoff, on spectrum analysis, was probably his greatest contribution to science. These researches opened up an entirely new field of chemistry, for not only could very small quantities of the known elements be easily detected by these methods, but unknown elements could be detected by its aid, as Bunsen and Kirchhoff showed shortly afterwards when they discovered cesium and rubidium, elements so similar to potassium and sodium that they had previously been mistaken for them; and, as has been more recently shown, in connection with the discovery of argon, helium, and other gases occurring in the atmosphere. Through the aid of spectrum analysis not only the composition of the stars but even the nature of their motion can be determined. The methods for the detection and estimation of gases as devised and arranged by him have been found so precise and thorough that only trifling changes have been made in them. His work on the geological conditions of Iceland and on geysers and volcanic rocks led to very important new views on this subject. It was only after the work of Bunsen and his followers on the nature of the gases and products formed in an explosion of gunpowder that the nature of the process was understood, and his work on furnace gases led to a much clearer insight into the chemical processes taking place there. These lines of investigation, besides such as his important study of the chemical action of light and of specific heats, are sufficient to show what an impetus Bunsen gave to every line of investigation which he undertook. To the world at large he is perhaps best known as the designer of the burner and battery which bear his name. He was the

author of a number of scientific works and a member of many scientific societies. He was awarded the Copley medal in 1860, and in 1877 was, jointly with Kirchhoff, the first recipient of the newly-instituted Davy medal. With the exception of his eyesight, which was slightly impaired, he retained his faculties to the end. J. E. G.

REVIEWS.

THE FUNDAMENTAL LAWS OF ELECTROLYTIC CONDUCTION. EDITED BY H. M. GOODWIN, Ph.D. Harper and Brothers. 1899.

This is one of Harper's Scientific Memoirs now being published under the editorial supervision of Professor J. S. Ames, of the Johns Hopkins University. The general scope of the series has already been outlined in this JOURNAL, **21**, 539. The present volume contains reprints of the papers entitled "Relation by Measure of Common and Voltaic Electricity," and "On Electrochemical Decomposition," by Michael Faraday; and translations of the following papers, "On the Migration of Ions during Electrolysis," by W. Hittorf and "On the Conductivity of Electrolytes Dissolved in Water in Relation to the Migration of their Components," by F. Kohlrausch. The book also contains the usual biographical sketches of the authors of the papers and a bibliography of the most important articles pertaining to these subjects.

J. E. G.

THE RISE AND DEVELOPMENT OF THE LIQUEFACTION OF GASES. BY WILLETT L. HARDIN, Ph.D. Harrison Senior Fellow in Chemistry in the University of Pennsylvania. New York. The Macmillan Company. 1899. 250 pages. $1.50.

This book will be very acceptable to those, and there are many such, who have occasion to study the history and development of the liquefaction of gases. The great interest in this subject, that has been aroused by the preparation of liquid air in large quantities and the liquefaction of those gases which have for so long resisted all attempts in that direction, has given rise to numerous articles on this subject written in a popular style. Much of the material is contained in journals not accessible to the general reader and the author has collected and arranged it in the form of a connected chronological treatise. After a general treatment of the historical and theoretical side of the problem, the experiments of Cailletet and his successors are described in detail with diagrams of the apparatus used. The author wisely refrains from any expression of opinion on the Dewar-Hampson-Linde-

Tripler priority claims. While the book is written in a popular-science style, sufficient details are given for all purposes except those of the specialist and he will probably have access to the original articles, to which full references are given. The book is thoroughly up to date and contains the results of work done up to April 1899.

J. E. G.

GRUNDRISS DER ALLGEMEINEN CHEMIE. VON W. OSTWALD. Mit 57 Textfiguren, Dritte, Umgearbeitete Auflage. Leipzig: Verlag von Wilhelm Engelmann. pp. 549. 1899.

The earlier editions of Ostwald's "Grundriss" have done more to arouse an interest in the elements of physical chemistry, than any book ever written. This applies not alone to readers of German, since we have been so fortunate as to have at our disposal an admirable English translation by Dr. Walker. The third edition has been prepared for the purpose of incorporating the work of the last ten years. It has been rearranged and enlarged, until it almost amounts to a new book, changes and additions having been made at every turn.

The new edition, like the old, is divided into twelve books, but the order is by no means the same. Book one, deals with mass; the conservation of mass, the laws of definite and multiple proportions, the conception of an element and atomic weights, including most of the recent atomic weight determinations, and the relations between the atomic weights as brought out by the periodic system. Books two, three, and four, are on the stöichiometry of gases, liquids, and solids, respectively. Book five, on dilute solutions is, of course, of special interest. Chapters are devoted to osmotic pressure, diffusion, vapor-pressure of solutions, freezing-point of solutions, and salt solutions. The Beckmann boiling-point and freezing-point apparatus, should always be given a prominent place in connection with these methods, because these are the fore-runners of all that has been done. But both of these methods, and especially the apparatus used in carrying them out, have been so greatly improved, that it would seem that the value of these chapters would have been increased by a brief reference to the newer work.

Book seven, on systematics, contains chapters on the choice of combining weights, the periodic law, the molecular theory, and the theory of chemical compounds. These seven books constitute the first part of the volume, which, as a whole, is known as *stöichiometry*.

The second part of the volume, on *affinity*, takes up the various energy transformations, and includes book seven, on thermochemistry, book eight, on chemical mechanics, book

nine, on electrochemistry, book ten, on photochemistry, and book eleven on methods of measuring chemical affinity.

There is, perhaps, no portion of the work as much enlarged as that which deals with electrochemistry. This is due to the unusual activity which has manifested itself in this field during the past few years. The order of treatment here, is very much the same as in the *Lehrbuch*: The law of Faraday, conductivity, properties of ions and electromotive force of elements. A chapter has also been introduced on electrical equilibrium.

In this third edition of the "Grundriss," we are provided with an elementary treatise, covering the whole field of physical chemistry. The work needs no comment, since it comes from the one who has done more than all others to systematize the newer developments, and found the modern school of physical chemistry. An English translation of the book would be welcomed by those who are not familiar with German.

H. C. J.

OUTLINES OF PHYSICAL CHEMISTRY. By A. REYCHLER, Professor of Chemistry in the University of Brussels. Translated from the French, with the Author's permission, by John McCrae, Ph.D., Demonstrator of Chemistry, The Yorkshire College, Leeds. With 52 Illustrations. Whittaker and Co., London. Macmillan, New York. pp. 271. 1899.

The large number of elementary books upon one chapter or another of physical chemistry, is but an expression of the growing interest in this branch of science. Among these, the little book in hand deserves a prominent place. The subject is treated in a much broader way than is common in an elementary work, and a sharp feeling for the relative importance of things is manifested throughout.

The book begins with a reference to the fundamental laws of chemical action and the laws of weight, and of definite and multiple proportions, and this is followed by a brief discussion of the density of gases, and methods for determining their molecular weights. A short account of the constitution of molecules and of Mendeléeff's classification of the elements is given, and then chapters follow on the stöichiometry of gases, liquids, and solids. The third part of the work deals with thermochemistry, electrochemistry, and the nature of salt solutions. The fourth and last takes up problems in chemical equilibrium, chemical dynamics, and hydrolytic dissociation.

We notice that in a few places the more recent work is not mentioned. Under the refracting power of liquids no mention is made of the work of Edwards. In the interesting chapter on optical activity and the Le Bel-van't Hoff hypothesis, the unique exception discovered by Baeyer should find a place.

The work of Rodger and Watson on magnetic rotation is of the highest importance, and should, at least, be ranked with that of Perkin. The freezing-point and boiling-point methods, devised by Beckmann for determining molecular weights, have been so far improved, that the original forms are hardly used at the present, and these methods have both been applied to a problem of greater interest and importance than that of determining molecular weights; *viz.*, the measurement of the dissociation of electrolytes in aqueous and non-aqueous solutions.

But it is impossible to include everything in a small, elementary, treatise, and we are impressed rather with the large amount of interesting and important material in this little treatise, than with the few omissions. The book is unusually clear and concise, and is very well illustrated. It is heartily recommended to any one who wishes to begin the study of physical chemistry.

H. C. J.

INDICATORS AND TEST-PAPERS. Their source, preparation, application, and tests for sensitiveness. A résumé of the current facts regarding the action and application of the indicators and test-papers which have been proposed from time to time, and are in present use in chemical manipulations. By ALFRED I. COHN, PH.G. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1899. 249 pages. Cloth, $2.00.

The author has collected from all available sources the list of substances which have been suggested for use as indicators and test-papers and has arranged them in this book, the general nature of which is expressed upon the title-page.

J. E. G.